

# THE ADHESION OF FLAME AND PLASMA SPRAYED COATINGS

BY

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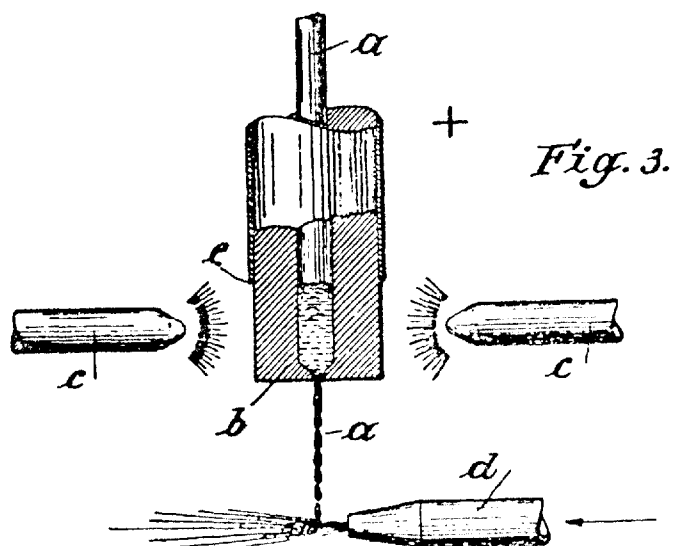
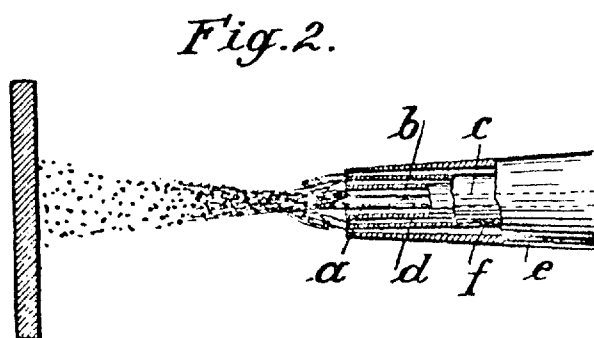
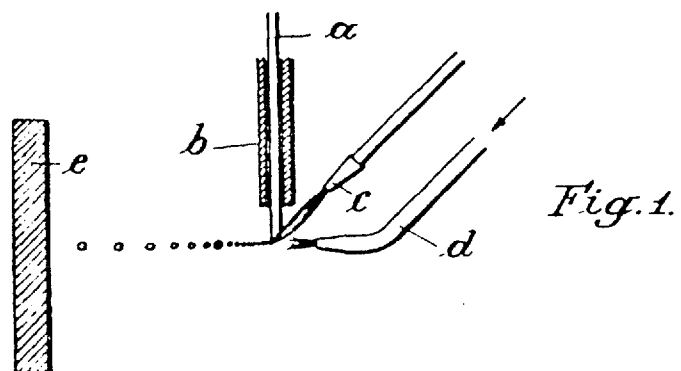
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"EARLY FORMS OF THE FLAME AND PLASMA SPRAYING PROCESSES"

from British Patent 28,001 4th December  
1912, by E. Morf: titled "A Method of  
Producing Bodies and Coatings of Glass  
and other Substances".



Hermann Hesse in *The Glass Bead Game* describes the young scholar Joseph Knecht who aspires to learn the intricacies of "the Game" from his Music Master. Hesse writes -

*"The Game as I conceive it," Knecht once wrote to the former Music Master, 'encompasses the player after the completion of meditation as the surface of a sphere encompasses its centre, and leaves him with the feeling that he has extracted from the universe of accident and confusion a totally symmetrical and harmonious cosmos, and absorbed it into himself."*

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## SUMMARY

A number of aspects related to the adhesion of flame and plasma sprayed coatings is examined in this thesis. In particular the properties of plasma sprayed coatings depend on:-

- (i) the design of the plasma torch and the processes that occur within it,
- (ii) the temperatures and velocities of the individual particles which form the coating, and
- (iii) the coating structure.

These factors influence the adhesion of the deposit to the substrate and this is, in turn, reflected by the testing method of determining the adhesion. Therefore this thesis contains four sections of research and these are summarised below.

A plasma spraying system was manufactured and the design of torches investigated (Chapter Two). The torch design is dependent on the voltage-current characteristics of the power supply because these fundamentally determine its operating range. In the case of this work it was found that the maximum stable operating power was about 22 kW when using an argon/nitrogen work gas mixture, and that this power was not adequate to spray ceramic materials.

Chapter Three examines a photographic technique, based on the principles of two colour pyrometry, which was used to determine the temperature and velocity of particles as a function of their distance from the torch exit. However the resolution of this method was largely dependent on the response of the photographic film to the radiation emitted by the particles; so that the results detailed in this work are only qualitative. In general the results agree with the simple theory that particles cool and slow down as they move away from the torch.

The structure of plasma sprayed coatings was characterised as consisting of flattened droplets which physically interact to form a dense deposit. Both metal and ceramic coatings exhibited similar morphological features such as dendrites and columnar grain growth; and these results are described in Chapter Four.

The adhesion of plasma sprayed coatings to a substrate is usually measured by carrying out a tensile adhesion test. The limitations of this method are explained in Chapter Five.

Chapter Six therefore investigates an alternative testing method which is based on the principles of fracture mechanics. In this way the fundamental material property of crack extension force is used to describe the adhesion of coatings. Both the double torsion (DT) and double cantilever beam (DCB) testing methods were used; however the DCB was the most suitable and is described in detail. Coatings of mild steel, nickel-aluminium, alumina-titania and a composite coating of nickel-aluminium and alumina-titania, all sprayed onto a grit blasted mild steel substrate, were examined in this way and the fracture toughness related to the fracture morphology. Cohesive or adhesive failures were promoted by grooving the specimen and thus the failure mechanism which limits the overall coating integrity was established. It was observed that high adhesion of the coating was related to large deformation of the individual lamellae within the coating. In this way it was possible to explain how adhesion of a ceramic coating can be increased by incorporating a nickel-aluminium sub-coat.

## DECLARATION

To the best of my knowledge and belief,  
this thesis contains no material previously  
published or written by any other person,  
except where due reference is made in the text.  
It does not contain any material which has been  
accepted for the award of any other degree in  
any university.



Christopher C. Berndt

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It is with great pleasure that I acknowledge the supervision of Associate Professor R. McPherson. Reg kept in touch with the progress of the research and always managed to keep the main aim of the work in perspective despite several "red herrings". His advice and free thought are appreciated - although they were not always followed.

The research was mostly carried out in the Department of Materials Engineering and Professor Ian Polmear is thanked for providing these facilities; as he also is for being my temporary supervisor during part of my candidature.

All phases of the project relied heavily (if not completely) on the backup support of the technical personnel within the department. Most of the equipment and all of the fracture toughness specimens were manufactured within the department workshop; and this is under the direction of Mr. Bruce Young. In particular I wish to praise the excellent (if not fastidious!) workmanship of Messrs Jim Hobson and Peter Slater who together produced the gas control unit, various benches and numerous torches. Peter managed to translate my engineering drawings into operating torches and often implemented practical modifications to their construction. Mr. Ken Bride always made his engineering abilities available and often managed to find at least two simple ways to solve some frustrating minor problem.

A section of the experimental work entailed extensive trials using photographic techniques and Julie Fraser, the departmental photographer, contributed her considerable skill and practical knowhow during this phase of the work. Mr. E. Dixon of Kodak (Australasia) assisted with the sensitometric interpretation of the film and provided the basic data so that an analysis could be carried out. The micro-density measurements were carried out at C.S.I.R.O., Chemical Physics Division, Clayton.

The electron microscope was driven under the guidance of Karl Richter and his patience and technical skills are appreciated. Mr. Bob Mitchell introduced me to using computer methods for data acquisition and analysis. Modifications of his "patching" and basic programmes were taken advantage of to a great extent.

Contributions to the ideas incorporated within this thesis have been derived from discussions with former colleagues and members of the staff. In particular Raju and Kevin helped me assess the fracture toughness methods.

Financial assistance during the tenure of the project was provided by the Australian Welding Research Association (under Contract 52), and additional funds via The Ian Potter Foundation and the Dutch Government allowed me to attend the 9th International Thermal Spraying Conference, Den Hague in May 1980.

The presentation of this thesis owes much to the typing skills of Bev - a really great job! Julie lent considerable service ("beyond the call of duty") in the reproduction of line drawings, photo-set pages and photographs. Finally Steve and Ursula provided me with nourishment and warmth for the final months during the preparation of this thesis - and this was terrific!

# CHAPTER ONE

## INTRODUCTION

### 1.1 THERMAL SPRAY COATINGS

Thermal spray coatings are produced by melting and projecting a material so that a stream of droplets impacts against a substrate and builds up a surface coating (Hoffman, 1978; Mock, 1966; Gerdeman and Hecht, 1972). There are two well established techniques used to prepare coatings in this manner and these are termed flame spraying and plasma spraying.

In both cases the specific properties of the coating material are imparted to an engineering component to take advantage of their thermal, wear or chemical resistance. Thus a ceramic mixture of alumina and titania can be coated onto rocket nozzles and exit chambers of rocket engines to provide heat insulation of the underlying metal structure and also to enhance the abrasion resistance to fine particles. Tungsten, molybdenum and tantalum have also been used as refractory coatings whereas copper is used to provide electrical and thermal conductivity. Coatings of aluminium are used to protect iron and steel against atmospheric and aqueous corrosion while carbides (Cr, Mo, Ta, Ti, W) and nickel base alloys are commonly used for hard facing components. Thermal spray coatings have also been applied to reclaim worn components and in the manufacture of articles by spraying onto a preform which is later removed.

Composite thermal spray coatings consisting of different materials are most useful and can be manufactured by:

- (i) mechanically mixing the individual components as powders;
- (ii) thermal spraying each powder to form several discrete layers or,
- (iii) chemically treating the powder prior to spraying so that a composite powder is produced which consists of a core of one material enveloped in the other.

A particularly important member of this latter class of powder is Al-Ni which has the advantage of strong adhesion to a prepared substrate, and also provides a base to which ceramic coatings adhere well. These coatings are termed "bond coatings" and are usually applied prior to spraying a ceramic coating.

## 1.2 THE THERMAL SPRAY PROCESS

The flame spraying process is the most well known and originated in about 1910. The method derives heat from the combustion of oxygen and acetylene in a specially designed torch in which the deposition material is carried through the hottest region of the flame. The velocity and temperature of a particle is limited by the properties of the flame to about  $300 \text{ m sec}^{-1}$  and  $3400^\circ\text{K}$  (Scott, 1974). Plasma spraying, on the other hand, makes use of gas heated by a constricted direct current arc in apparatus which is shown schematically in Figure 1.1. A high intensity arc is established between a cathode and anode so that when suitable gas is passed through the torch it is formed into a plasma.

The plasma gas consists of a mixture of partly dissociated gas molecules, ions and electrons and a great advantage of the plasma is that a large amount of heat is available at high temperatures ( $5000$  to  $15000^\circ\text{K}$ ) by the recombination of dissociated diatomic gases. This means that rapid heat transfer is possible to particles injected

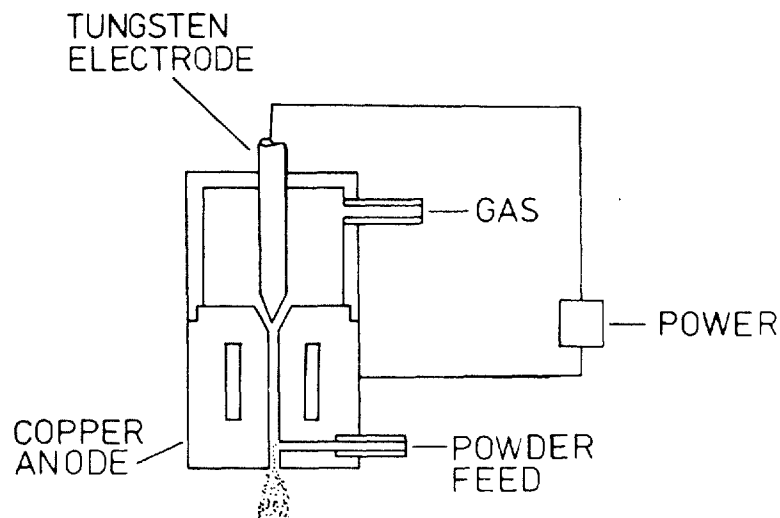


Figure 1.1: Schematic Diagram of a Plasma Torch and System

into the gas stream and high melting point materials may be melted and accelerated to a high velocity ( $600 \text{ m sec}^{-1}$ ) in their very short residence time. The gases used are limited to those which do not react with the tungsten cathode; usually mixtures of argon, nitrogen, helium and hydrogen.

### 1.3 SCOPE OF THE PRESENT STUDY

The technology of plasma spraying has evolved empirically from experiment. To achieve any further improvements in the process it is necessary to understand the full range of operations encompassed by the plasma spraying process and these are detailed below. It is also most important to measure how well a coating adheres to a substrate if improvements are to be made and special emphasis is devoted to this topic.

Therefore the present work examined four broad aspects from a fundamental viewpoint.

- (1) The torch design was investigated by building several different torches and plasma spraying systems (Chapter 2). The plasma spraying system developed however could not spray ceramic materials satisfactorily because of limitations associated with the power supply.
- (2) The temperature and velocity histories of the particles on impact with the substrate were examined (Chapter 3) because these properties control the nature of bonding in the coating and between the coating and substrate. The method used was based on two colour thermography.
- (3) The coating surface and profile (the plane perpendicular to the substrate) were examined by electron microscopy and characterised as consisting of flattened droplets which interact to build up a deposit. Also samples produced by the controlled fracture of specimens were studied in the region of the substrate-coating interface and the bulk of the coating. These results are presented in Chapter 4 and agree with the observations presented in the literature concerning the structure of flame and plasma sprayed coatings.
- (4i) The tests generally used for measuring the adhesion of a coating were examined and the tensile adhesion test studied in detail. This test was not considered satisfactory as a quantitative method of measuring the coating adhesion and the reasons for this are presented in Chapter 5.
- (4ii) A major part of the work involved the development of a fracture mechanics test to determine the "effective" adhesion of a coating (Chapter 6). Different fracture modes (adhesive and cohesive) of plasma sprayed coatings were also examined. These tests were successfully used to determine a parameter related to the adhesion of metal (mild steel and nickel-aluminium composite) and ceramic (alumina-titania) coatings to a mild steel substrate. The fractography of coatings was examined and related to the fracture toughness

for cohesive and adhesive failure, and a new explanation of the role of metallic bond coats in improving the adhesion of ceramic coatings is proposed.

## CHAPTER TWO

### DESIGN OF PLASMA SYSTEMS

#### 2.1 LITERATURE SURVEY

##### 2.1.1 INTRODUCTION

A plasma can be defined as an electrically neutral gas consisting of atoms and molecules which have been partially dissociated into positive nuclei and electrons. This process occurs when electrical energy is transferred to the gas so that the temperature is raised to approximately  $10,000^{\circ}\text{K}$  (Reed, 1967) and the process is further assisted by lowering the pressure. The high temperature of the plasma together with its high thermal conductivity, enthalpy (Figure 2.1) and in some cases inert character can be used to rapidly heat materials or carry out reactions.

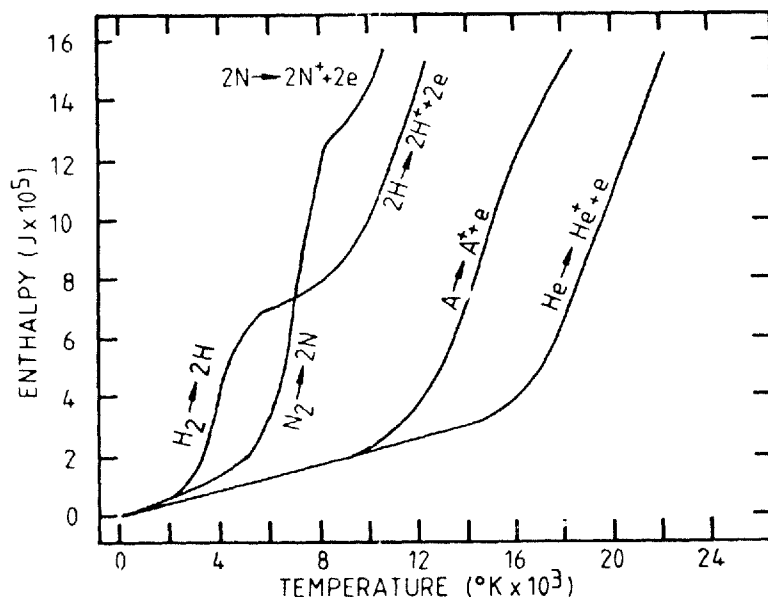


Figure 2.1: Enthalpy-temperature curves for plasma forming gases (Baddour and Timmins, 1967b).

Plasmas are broadly classified below according to their origin.

- (1) *r-f plasmas* - The gas is passed through a radio frequency field so that electrical coupling occurs and energy is transferred to the gas.
- (2) *DC plasmas* - The gas is used as a medium in which a direct current arc is established between two or more electrodes.

The main advantage of the r-f plasma is that no electrodes are necessary for its generation and thus no contamination of the working gas or materials injected into the plasma occurs (Reed, 1961; Marynowski and Monroe, 1964). However this thesis is more concerned with the DC plasma and the following discussion is restricted to their generation and characteristics.

DC plasmas that operate between  $10^{-1}$  to  $10^{-5}$  amps are termed "glow discharges" and should be distinguished from higher current ( $> 10^{-1}$  amps) "arc discharges". The gas discharge system consists of two interacting systems (Baddour and Timmins, 1967b). The first system contains electrons which initially gain energy from the electric field and transfer it via collisions to the second system of neutral molecules, ions and molecular fragments. Thus the temperature of the plasma can be defined in terms of the electron or gas temperature and these reach equilibrium at about one atmosphere. Therefore at low pressures, where glow discharges operate, the electron temperature is much higher than the gas temperature and the plasma is termed a "cold plasma". On the other hand in the regime of arc discharges the gas temperature is more dominant and a "thermal plasma" is said to be formed.

The arc of a thermal plasma can be produced between two electrodes which are :

- (i) both contained in an integral unit, or alternatively
- (ii) the arc can be transferred from the cathode electrode (negative potential) to a work piece (at positive potential) in a process similar to welding.

The former "non-transferred" arc has the advantage (O'Brien, 1968) that much higher temperatures are produced and this is used in several applications.

The high power range possible in thermal plasmas (up to 5 MW) has been used to simulate the re-entry environment encountered by rockets and missiles (John and Bade, 1961) whereas the middle range thermal plasmas (100 to 500 kW) are used for processing and refining materials (Sayce, 1976; Rykalin, 1976). Thermal plasmas of energy less than 100 kW are used for spraying and cutting applications and the present work will be confined to these.

A simplified diagram of the torch configuration for a DC, non-transferred arc, thermal plasma torch is shown in Figure 2.2 and the various components are featured. Normally a gas is forced under pressure into the arc chamber but most recently (Borer et al., 1976; Thalmann et al., 1976) power levels of 200 kW have been obtained by using a vortex of liquid (water, methanol, or water and ethanol) in the arc chamber to establish a stable arc. The major advantage of this

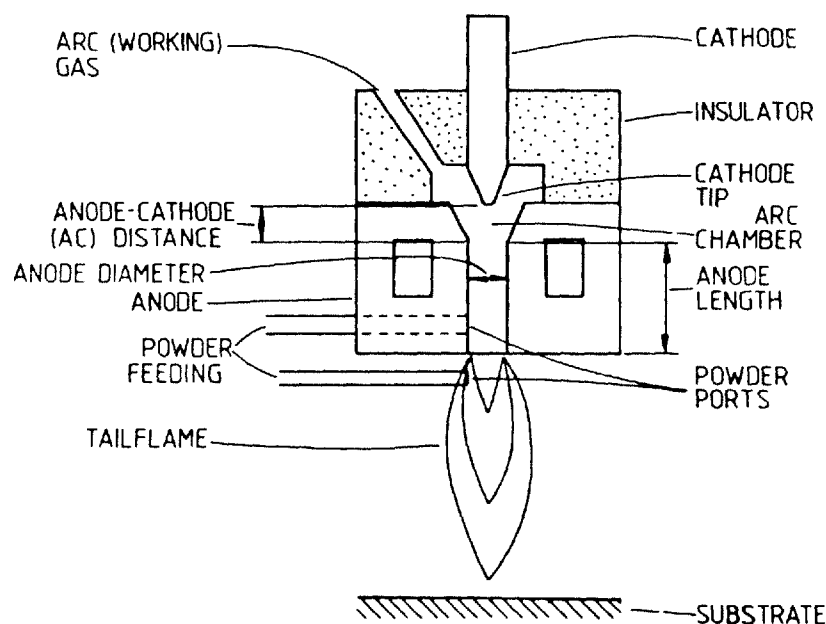


Figure 2.2: Components of a plasma torch

design is the high deposition rates of typically  $30 \text{ kg hr}^{-1}$  at a deposition efficiency (D.E. = weight of deposit  $\times$  100/weight of powder transported to the torch) of 55 percent compared to about  $3.2 \text{ kg hr}^{-1}$  at a deposition efficiency of 40 percent (Metco, 1978) for commercial equipment. The following sections are concerned only with the operation of the more popular gas stabilised, non-transferred arc, thermal plasma torches used for plasma spraying applications.

Stable operation of a plasma torch depends on the arc behaviour and this in turn is related to the gas flow in the arc chamber. The two main methods (Gerdeman and Hecht, 1972, pp.6-8) of stabilisation in reference to this work involve feeding the gas either tangentially into the chamber to create an intense vortex or, introducing the gas from behind the rear electrode to create a gas sheath. Modern plasma spraying torches rely on an intense vortex being formed, at the cathode tip, which contains the arc as it travels down the front of the anode. The tangential gas flow also provides a relatively cool gas layer around the plasma jet which reduces the heat transfer to the front electrode (anode). The main function of the gas chamber and nozzle is to constrict the arc. Constriction increases the enthalpy and temperature of the plasma gas and results in the thermal pinch effect; the gas moving near to the walls of the anode is cooled and thus has a lower ionisation and electrical conductivity. The discharge current is therefore concentrated in the central zone of the effluent increasing the density, temperature and conductivity of this zone.

### 2.1.2 Plasma Torch Design

The basic components of all DC plasma torches suitable for spraying incorporate the following features (Figure 2.2).

1. A thoriated (1-2 percent) tungsten electrode. Thorium is used to lower the work function (or electron emission threshold) from 4.52 eV (for pure tungsten; Weast, 1974, p.E82)

to 2.63 eV (Gross et al., 1968, p. 247) and allows an arc to become established at a lower voltage gradient.

2. A copper anode which also incorporates the nozzle or anode throat. Allowance can be made to inject the powder directly into the nozzle but in the more common design the powder is injected into the plasma tailflame.
3. An insulating medium such as teflon or ceramic between the cathode and anode which forms the arc or gas chamber.
4. A torch body to join and align the above components into an integral assembly.
5. Attachments for water lines and power cables.

The anode and cathode have a limited life of from 20 to 200 hours (Gross et al., 1968, pp. 295,312) depending on the power level at which the torch is operated. It should be kept in mind that these components must be replaceable and any seals incorporated in their design must be completely water tight since a leak within the cooling circuit will lead to rapid erosion of the anode and cathode.

Many references (Andrews, 1974; Brossard et al., 1964; Brzozowski and Celinski, 1962; Fauchais, 1968; Gross et al., 1968, pp.232-324; John and Bade, 1961; Nachman, 1973; O'Brien, 1968) detail the geometry and material requirements of a plasma torch and relate these properties to the operating characteristics. Fauchais (1968), Brossard et al. (1964) and Brzozowski and Celinski (1962) carried out experiments with torches constructed in modular form which allowed the dimensions of the arc chamber and anode to be changed. Relationships were established between the physical dimensions of the torch, the voltage gradient, gas pressure within the torch, torch power and efficiency. The torch efficiency is defined as the fraction of power contributed to the gas (sometimes referred to as the gas enthalpy) and is calculated by considering the heat losses to the cathode and anode. The major results with reference to this work are:

1. The arc voltage and torch power increases with an increase of the anode-cathode distance, the anode diameter and length, and the gas flow rate.
2. The voltage and current characteristics can be changed by modifying the shape of the arc chamber but the most convenient manner is by varying the nature of the working gas; for example the voltage and current can be increased by using a diatomic gas such as nitrogen or hydrogen in preference to a monatomic gas.

Specific recommendations concerning plasma torch design have been made (Nachman, 1973) by initially selecting the working gas and then finding both the power supply requirement and the resultant torch power rating. If the voltage gradients in regions of the anode, cathode and column are known then the maximum working current and minimum working voltage can be calculated and compared to the characteristics of the power supply. The importance of matching the electrical characteristics of the torch and power supply are detailed in section 2.1.4. The maximum power dissipated at the anode wall is about 20 percent (Fauchais, 1968) and is related to the maximum current. If copper is used as the anode material then the internal dimensions of the anode can be calculated (Gross et al., 1968, pp. 287-289; Nachman, 1973) for heat dissipation at a maximum rate of  $10 \text{ kW cm}^{-2}$ .

The cathode dissipates 5-7 percent of the input power and its erosion rate increases with the power density. Several empirical relations have been derived (Nachman, 1973; Gross et al., 1968, pp. 282-287) which relate the cathode diameter and length to the maximum working current.

The geometrical relationship of the anode and cathode affects the mode of gas flow within the anode throat. As the cathode is moved into the anode throat the gas flow changes from lamellar to turbulent with the result that the establishment of an arc becomes more difficult and the torch power increases.

### 2.1.3 Arc Processes

The power of a DC circuit can be calculated from the Joule relation (voltage x current) but not all of this energy is contributed towards heating of the working gas or powders injected into the plasma tail flame. As the gas is heated to a temperature of approximately  $3900^{\circ}\text{K}$  (for  $\text{H}_2$ ) or  $7300^{\circ}\text{K}$  (for  $\text{N}_2$ ) the molecules of a diatomic gas initially dissociate into atoms (Gross et al., 1968, pp. 29-31) and then at higher temperatures ( $13000^{\circ}\text{K}$  and  $13500^{\circ}\text{K}$  respectively) ionise to produce an electrically neutral gas of positive ions and electrons - hence the term plasma. The fraction of gas that is ionised varies significantly with temperature (Andrews, 1974; Houben and Zaat, 1974a; Gross et al., 1968, pp. 31-38) and for argon reaches 50 percent at  $14500^{\circ}\text{K}$ .

The efficiency of gas heating is (Rykalin, 1976) 10-70 percent for argon and 30-80 percent for hydrogen. Only 5 percent of this energy is used to heat powders which are injected into the tail-flame whereas the contribution is 30 percent if powders are injected into the gas stream near to the cathode. It would be expected that the latter method of injection would be taken advantage of; but this leads to problems of powder decomposition at the very high temperatures as well as severe erosion of the cathode. The erosion can be substantially reduced by introducing the powder through a port near to the anode throat exit but problems arise with anode erosion and the build up of deposits within the anode.

The processes occurring within the torch are arc formation, growth and extinction (Jordan and King, 1965). Initially the arc is struck from the cathode, along the path of the ionised gas atoms, and is anchored at some point in the anode throat (Figure 2.3). The gas stream extends the arc into the shape of a hairpin and the discharge protrudes beyond the nozzle exit until the voltage drop along the discharge becomes greater than the breakdown potential between the arc column and the anode. The arc column then shorts circuits to the nozzle and the process repeats itself at a frequency of about 25 kHz.

The hairpin amplitude and frequency are dependent on the arc power and arc gas. For argon two or more hairpins which lengthen and short circuit independently can coexist whereas anode root splitting of this type does not occur in nitrogen arcs. The arc resistance is not uniformly distributed throughout its path (Andrews, 1974; Gross et al., 1968, p. 244) but varies according to Figure 2.4 where the voltage change is large in the anode and cathode fall regions compared to the relatively good conductivity along the arc column. If the anode and cathode voltage drops are known then the average voltage drop in the anode throat can be calculated and the voltage fluctuation related to the movement of the anode root. For example, Jordan and King (1965) found that the voltage gradient within an experimental torch was  $20 \text{ V cm}^{-1}$  and that the voltage fluctuation of 6-8 V corresponded to the track erosion within the throat over a distance of 4 to 3 mm (ideally 20/6 to 20/8 mm).

Much work has been carried out to determine the velocity and temperature profiles of a plasma and this will be examined in Chapter 3.

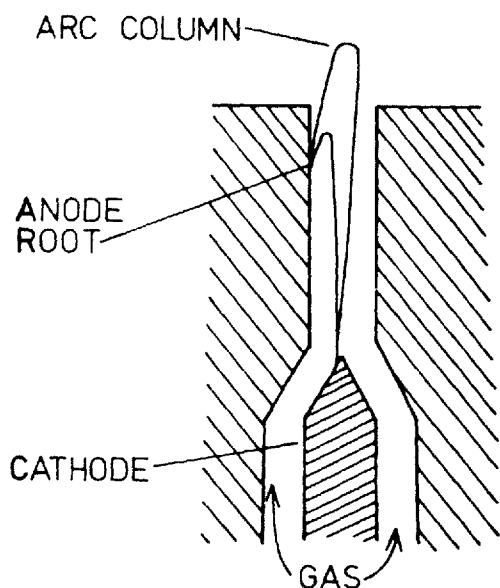


Figure 2.3: Arc formation and growth (Jordan and King, 1965).

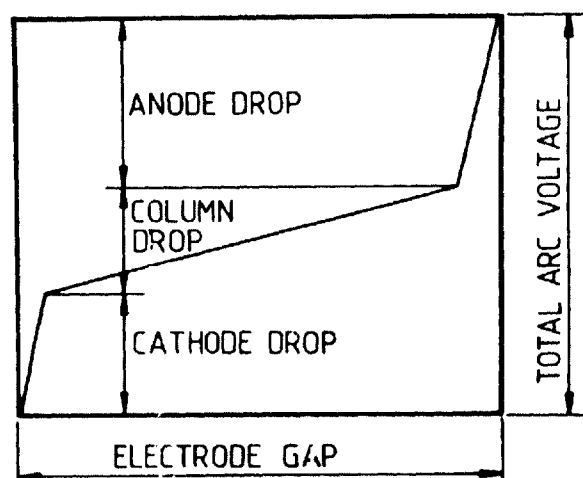


Figure 2.4: Arc resistance in a plasma torch (Andrews, 1974).

#### 2.1.4 Ancillary Equipment and Torch Operation

A plasma spraying system consists of the following components (Figure 2.5).

- (1) Plasma torch
- (2) Generator
- (3) Water cooling circuit
- (4) High frequency starting unit
- (5) Gas metering and control
- (6) Powder feeding.

The principles behind the operation of the plasma torch have been discussed in the previous section.

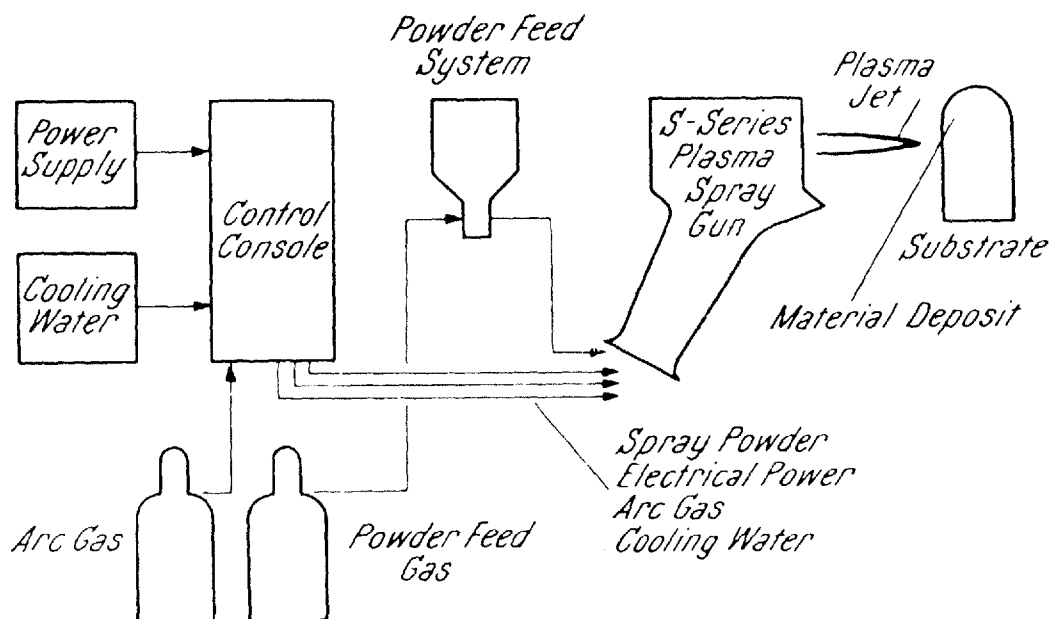


Figure 2.5: Components of a plasma spraying System (Gerdeman and Hecht, 1972).

The operating characteristics of a torch are given by the voltage-current relationships (Dunham, 1968; John and Bade, 1961; Andrews, 1974; Gross et al., 1968, pp. 241-243) and indicates the power level of the torch. The generator source is normally a silicon diode rectifier unit which incorporates a variable reactor to allow a range of drooping V-I (voltage-current) characteristic curves to be obtained.

The superposition of the arc and source characteristics allow the stable operating current and voltage of the torch to be determined (Figure 2.6). The arc can burn steadily where the arc voltage equals

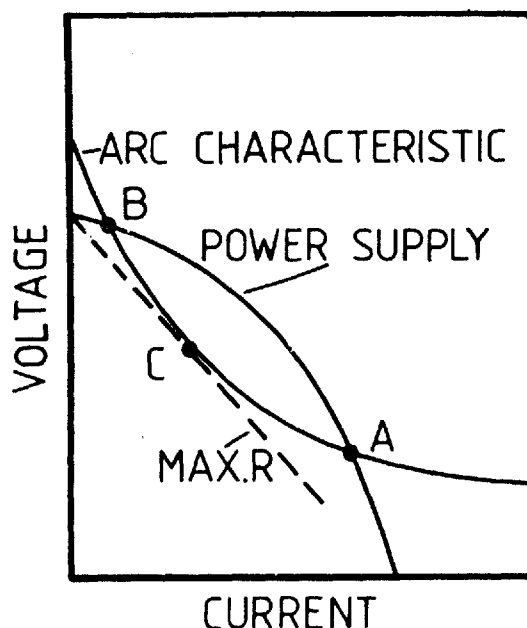


Figure 2.6: Voltage-current characteristics of a torch and power supply (Andrews, 1974).

the voltage across the source terminals; at points A and B. At point B any decrease in the current will extinguish the arc since the voltage requirement of the torch arc cannot be supplied by the generator. However if the current increases then the arc voltage decreases and an equilibrium point is reached at A. At this point any current change causes a voltage change which returns the current to point A. The torch resistance is given by the slope ( $V/I$ ) of the straight line in Figure 2.6 and if this decreases then the operating current increases. The maximum operating resistance of the torch is given by the tangent to the source characteristics; at point C.

Ideally the arc root should cover the largest possible area of the anode nozzle and this is where careful design of the anode dimensions in relation to the gas flow rate and gas injection mode must

be considered. If the gas velocity (controlled by the nozzle dimensions and gas flow rate) is low then the arc will not form or it may become localised onto the anode throat. However at high velocities no arc can be established or, if formed, the relative gas enthalpy is low (Figure 2.7).

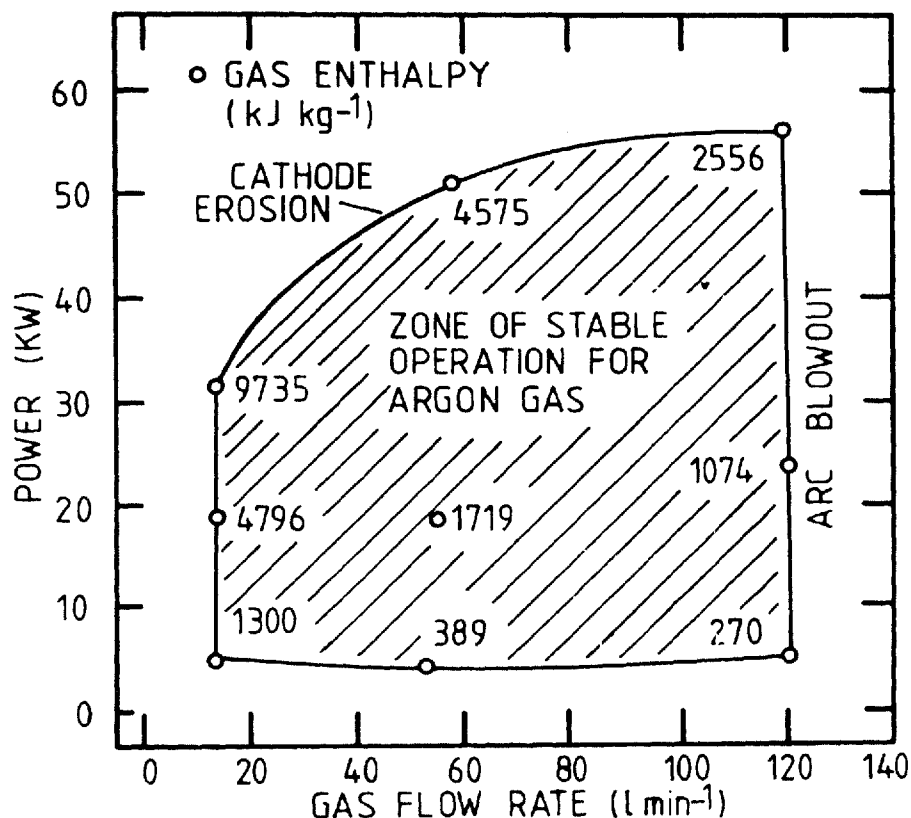


Figure 2.7: Operating range of a plasma torch with respect to gas flow, power and enthalpy (Gerdeman and Hecht, 1972).

The anode and cathode are water cooled and this must be efficient if electrode erosion is to be kept minimal. A large amount of energy is liberated at the anode due to the release of electron kinetic energy and copper is usually chosen as the anode material because of its high thermal conductivity. Power is usually supplied to the electrodes by means of a small diameter (7 mm) bare cable which is immersed in a fast flowing water stream (16 l min<sup>-1</sup> at 0.69 MPa,

Metco, 1978) . Safety circuits are usually incorporated into the cooling system and these prevent power supply to the torch unless there is an adequate water flow through the system.

The secondary of an air cored output transformer of the high frequency (HF) starting unit is connected in series with the power source and provides a high frequency discharge (about 1 M Hz) to initiate gas ionisation. After an arc is formed between the cathode and anode there will be a current surge and, following the voltage-current characteristics of the source and torch (Figure 2.6), the voltage will decrease. The current surge is commonly detected by a magnetic relay which in turn switches the HF unit off. Mixtures of gases are used to control the power level and arcing characteristics of a plasma spraying system. The arcing behaviour during the start up of a plasma torch is very severe so a monatomic gas is initially used because of its lower ionisation potential. Table 2.1 shows the dissociation and ionisation energies of some common plasma forming gases together with the average dissociation and ionisation temperatures. This data has been used (Houben and Zaat, 1974a) to calculate the enthalpy change with temperature as shown in Figure 2.1.

Table 2.1: Dissociation and Ionisation temperatures and enthalpies of gases.

|                | Dissociation                      |             | Ionisation                        |              |
|----------------|-----------------------------------|-------------|-----------------------------------|--------------|
|                | Enthalpy<br>kJ mole <sup>-1</sup> | Temp.<br>°K | Enthalpy<br>kJ mole <sup>-1</sup> | Temp.<br>K * |
| Ar             | 0                                 | -           | 363                               | 14500        |
| He             | 0                                 | -           | 567                               | 21500        |
| H <sub>2</sub> | 52                                | 3900        | 313                               | 13000        |
| N <sub>2</sub> | 113                               | 7300        | 336                               | 13500        |

\* Calculated from Saha's equation for 50% ionisation (Andrews, 1974)

The advantage of using a diatomic gas is that a large amount of energy is available at a low temperature so that particles can be heated up rapidly. Normally helium is avoided because of its high cost but this consideration is sometimes outweighed by its high thermal conductivity.

The essential feature of carrying powder to the torch is to regulate the powder entry into a moving stream of carrier gas (Fisher, 1972). The minimum flow of carrier gas is used since the gas cools the plasma tail flame yet at the same time this gas must support the maximum quantity of powder that can be melted by the plasma. Normally argon or nitrogen is used as the carrier gas at flow rates of approximately  $6 \text{ l min}^{-1}$  (Metco, 1978) and powder is deposited into this gas stream by:-

- (i) A rotary wheel which has grooves machined into its circumferential face. These grooves pick up the powder from the hopper outlet and deposit it into the carrier gas stream (Daley, 1970; Houben, 1976).
- (ii) A revolving screw which transfers the powder to the gas stream (Mash et al., 1961).
- (iii) A venturi arrangement whereby the flowing carrier gas creates a low pressure relative to the powder hopper with the consequence that the powder is forced into the gas stream due to the pressure difference (Gross et al., 1968, p. 373).

The deposition rate of powder onto the substrate varies from  $2 \text{ kg hr}^{-1}$  for alumina to  $16 \text{ kg hr}^{-1}$  for a nickel-aluminium composite powder (Metco, 1978). The particle size and distribution of the powder greatly affects the flow characteristics and the physical properties of the coating. Ceramic powders have a lower thermal conductivity than metal powders and the particle size of the powder must be relatively small for the particle core to melt.

A flowing powder entering the plasma flame will take one of the trajectories shown in Figure 2.8 (Fisher, 1972). The thermal history of particles taking these various lines of flight through the plasma flame can be calculated (Nachman and Gheorghiu, 1969; Scott and Cannell, 1967; Fiszdon, 1979) in order to establish the most appropriate operating conditions of a torch in conjunction with the physical properties of the powder to ensure complete melting. The theoretical calculations of particle velocity and temperature have not, as yet, been fully supported by experiments.

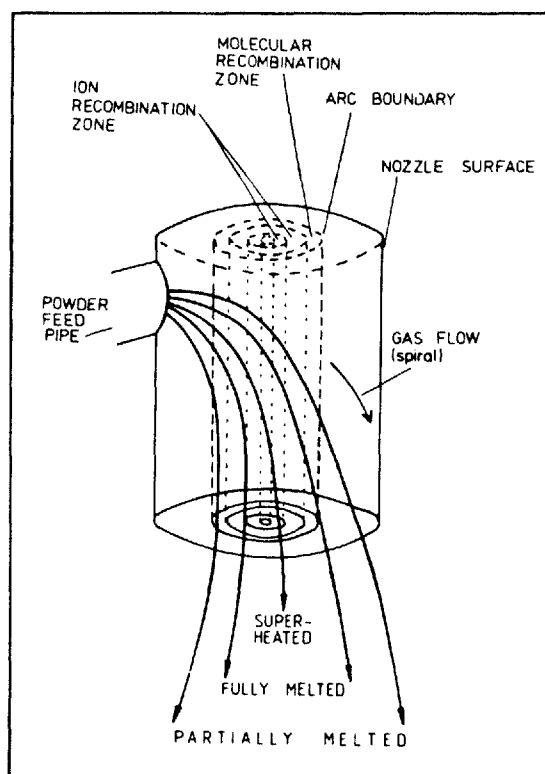


Figure 2.8: Possible particle trajectories in a plasma torch (Fisher, 1972).

High melting point materials such as ceramics have difficulty in reaching the molten state because they have both a short residence time in the flame, and (as fine powders) do not penetrate to the hot core of the plasma flame but appear to be deflected. Methods of alleviating this problem are to inject the powder counter current into the flame or to introduce the powder directly into the anode throat.

The literature concerning plasma spraying is incomplete in regard to the specific design considerations of plasma torches and ancillary equipment because this information has commercial interest and is often protected by patents. The patent literature (Appendix I) rarely contains technical details concerning the general operation of a torch but on the other hand publishes the geometry of the equipment and typical operating conditions. The following section details the design of a plasma system and presents results that were obtained.

## 2.2 SYSTEM DESIGN

### 2.2.1 Introduction

A plasma spraying system was constructed with the intention of producing coatings. The development of the system followed several stages:-

- (i) The design and construction of a plasma spraying unit capable of power levels of 16 kW.
- (ii) Modification of the torch to allow operation at high power levels .
- (iii) The incorporation of a semi-automatic operating console and high power (30 kW ) generator.

This section describes the design features of these components and presents results which detail the performance of the system.

### 2.2.2 Torch Design

During the course of this work several different torches were designed and constructed. Torch 1 (Figure 2.9) was used most

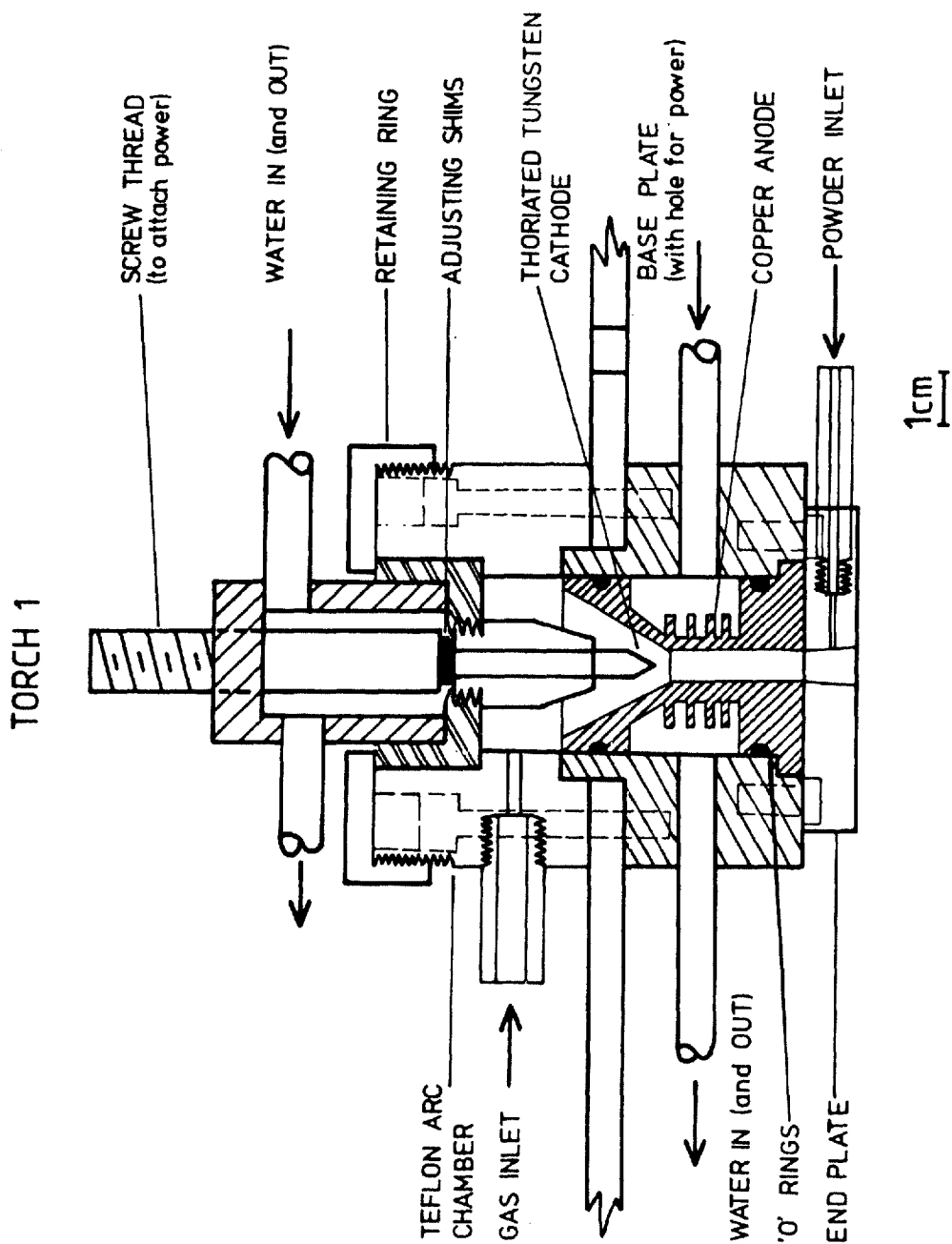


Figure 2.9a: Diagram of Torch 1.

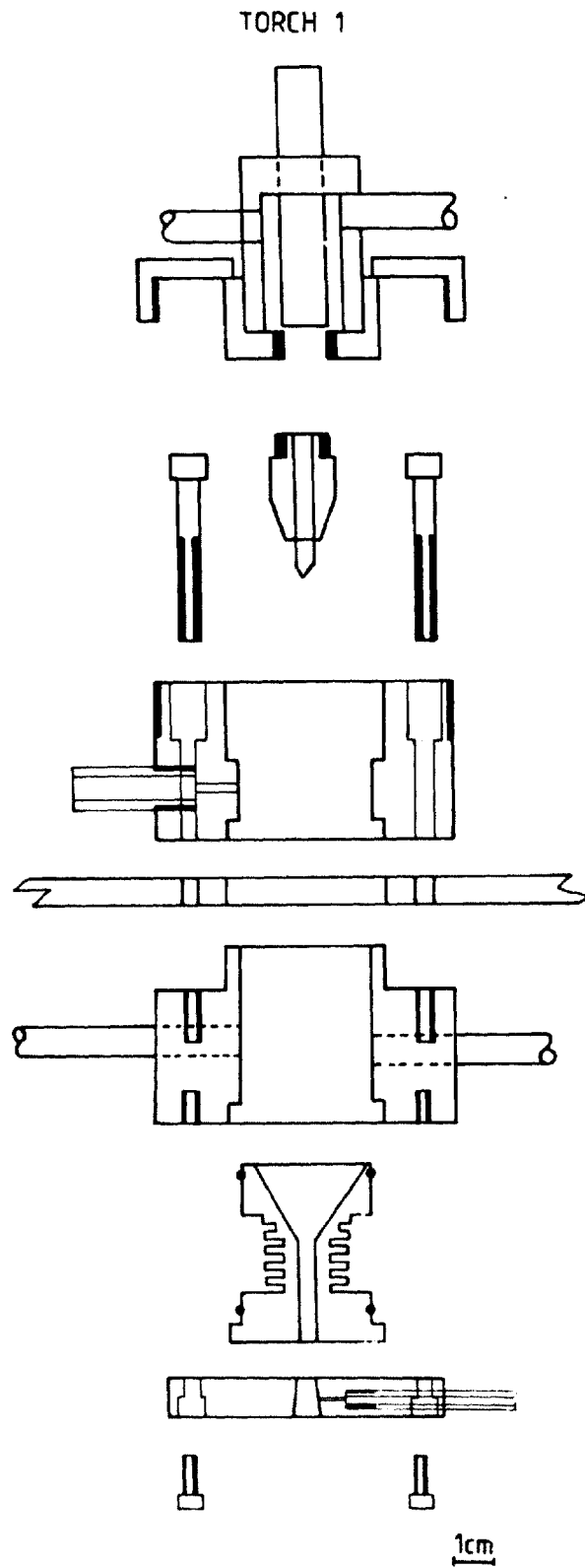


Figure 2.9b: Diagram of Torch 1 showing the various components.

frequently and did not suffer from the degradation problems that were frequently experienced with other torches.

The anode was made of copper and had a throat diameter of 6 mm with a length of 20 mm. The cathode was manufactured from 6 mm diameter W-2% Th and its tip ground to a  $60^{\circ}$  cone. The cathode could be positioned approximately 1.5 to 2.5 mm from the anode column by means of brass adjusting shims at the rear. The copper screw thread was not a satisfactory means of cathode adjustment due to deformation of the thread which in some cases led to water leaking into the arc chamber. The method of cathode and anode adjustment was then changed and is described below.

Water cooling was provided from the mains supply with no special precautions taken to increase the throughput by pumping. The teflon arc chamber maintained central alignment between the cathode and anode by incorporating recesses for both of these components. At the same time the teflon was remote from the arc processes and did not thermally degrade.

Further improvements were made to torch 1 to enable use at high powers:-

- (i) The tungsten cathode was made larger to decrease its average temperature and allow more efficient heat conduction to the water cooled copper body.
- (ii) Teflon spacers were used to increase the anode-cathode distance to a maximum of 8 mm.
- (iii) A teflon insert in the arc chamber was used to produce vortex stabilisation of the arc.

Modifications on the initial torch allowed easy dismantling of the cathode and anode to check for wear and also simplified their construction. The cathode of torch 2 (Figure 2.10) was an integral part which combined both water flow directly to the back of the tungsten tip and gas flow to the arc chamber. The gas was directed by the retaining ring to follow a tangential flow at the tungsten tip and this motion

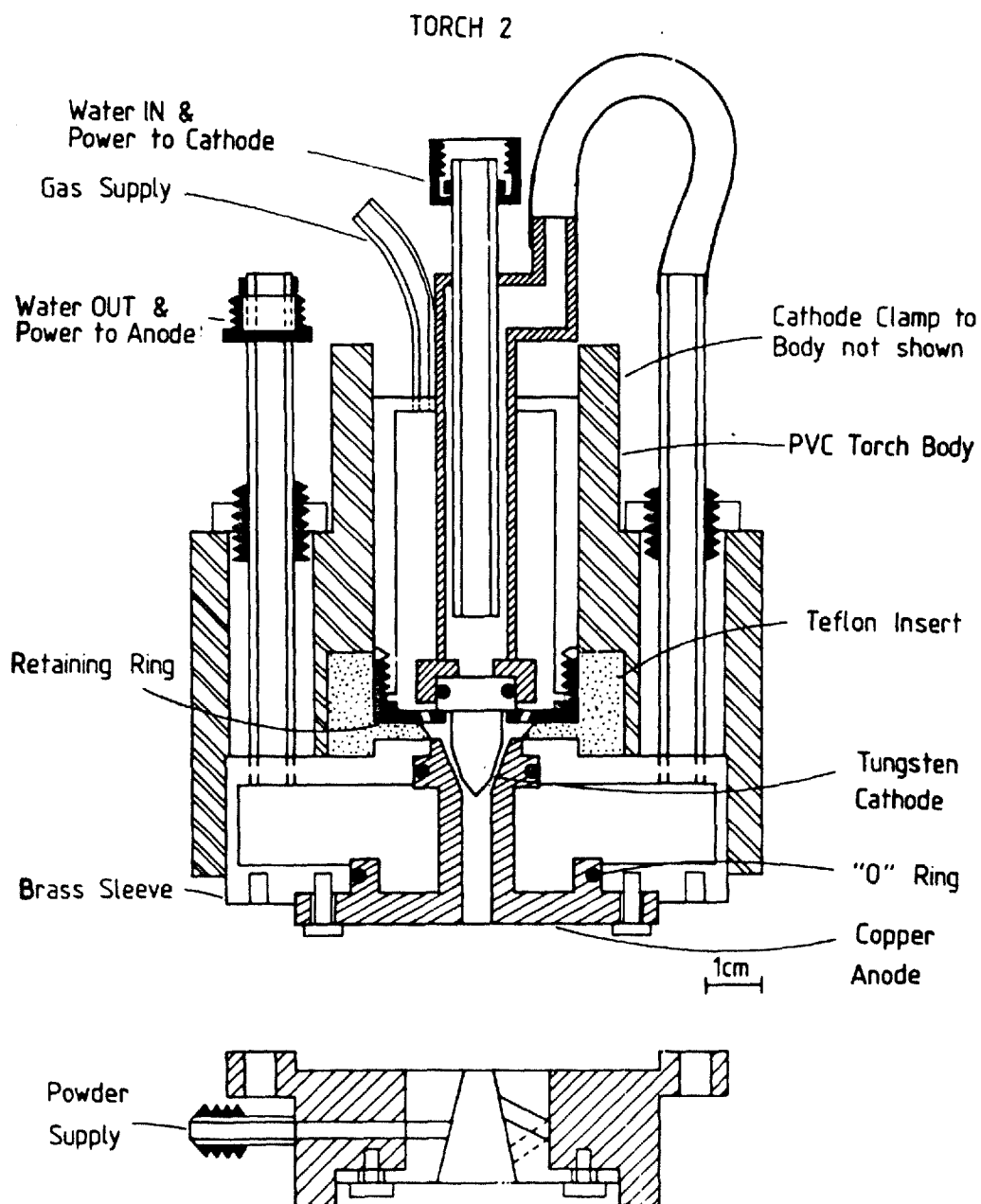


Figure 2.10: Diagram of Torch 2.

prevents an arc from becoming established between the cathode and anode throat.

The copper anode fitted into a brass sleeve which allowed water cooling. The "O" ring seals in the copper anode were dissimilar sizes for easy assembly. If these are the same size then the rear seal (closest to the cathode) must be forced past the front seal position and this is detrimental to its life. Both the cathode and anode fitted into opposite ends of a PVC body which had a teflon insert near the arc chamber region. The cathode was clamped into position whereas the anode was bolted rigidly to the torch body.

Both the anode and cathode were redesigned for torch 3 (Figure 2.11). The cathode assembly was simplified so that gas entered a chamber formed by the torch body and cathode prior to passing through the gas retaining ring. The anode was reduced in size although the dimensions of the anode throat (diameter and length) remained basically the same. The anode was held to the assembly by an anode cap which could also serve as a powder injection port. The cathode fitted through a PVC sleeve which flexed about two slotted areas when a clamping pressure was applied. This pressure resulted when the body cap was screwed onto the torch body. Arc gas entered the gas chamber via a hole through the cathode sleeve and it was therefore important to ensure that there were no leaks in this region.

Essentially the same cathode was used for torch 4 (Figure 2.12) except that a PVC cathode sleeve fitted under the gas cap and placed it central with respect to the anode. An "O" ring seal around the cathode sleeve prevented any gas leaks. Two cathode tips were also incorporated into the same fitting to simplify their manufacture. The distance between the cathode and the wall of the arc chamber was increased to minimise thermal degradation problems. The cooling cavity within the anode assembly was also fitted with a brass insert to increase the water flow velocity past the anode walls. The performance of these torches will be examined in section 2.2.4.

Several water cooled jackets were manufactured for placement over the anode exit with the aim of increasing the powder residence time

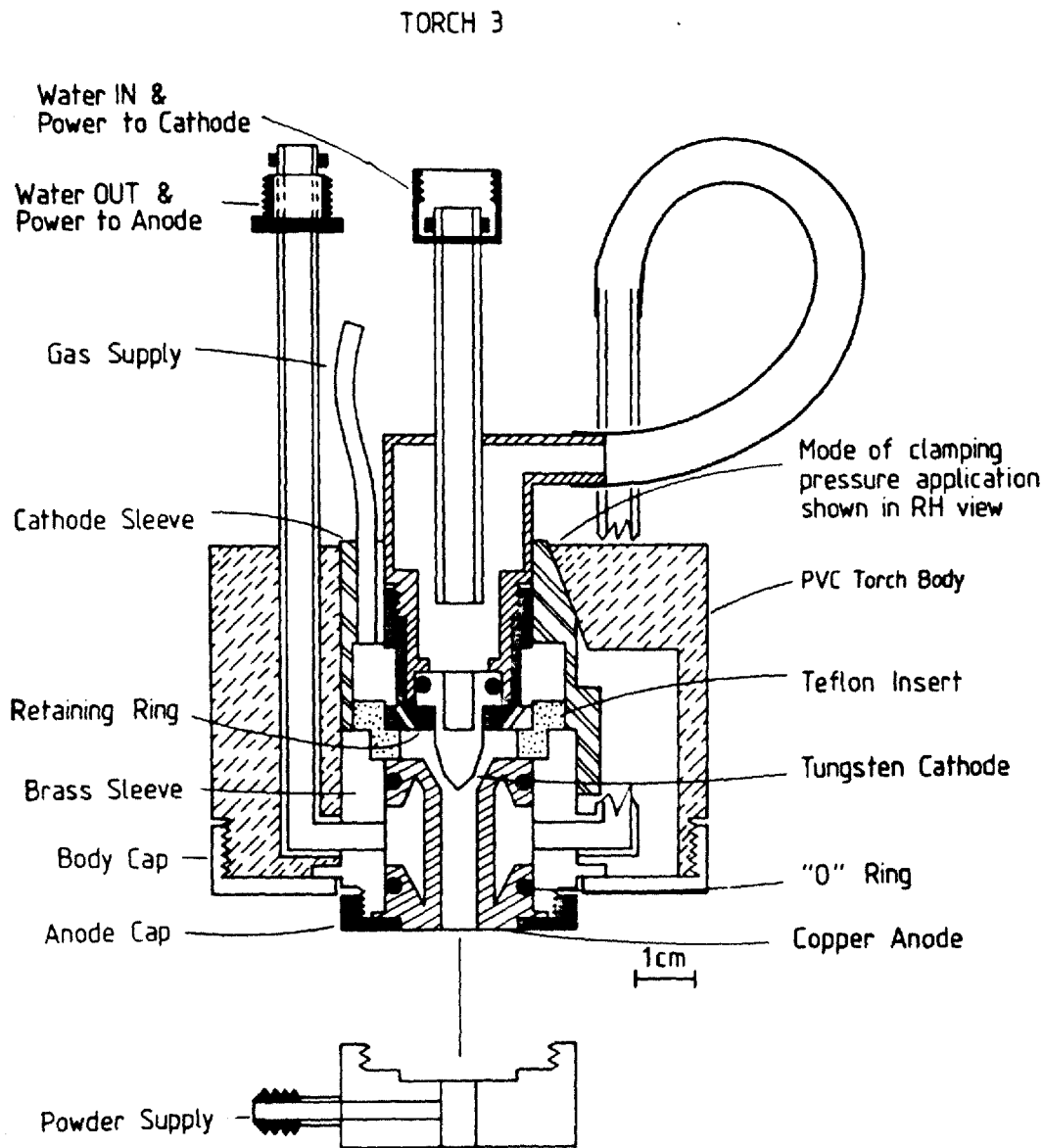


Figure 2.11: Diagram of Torch 3.

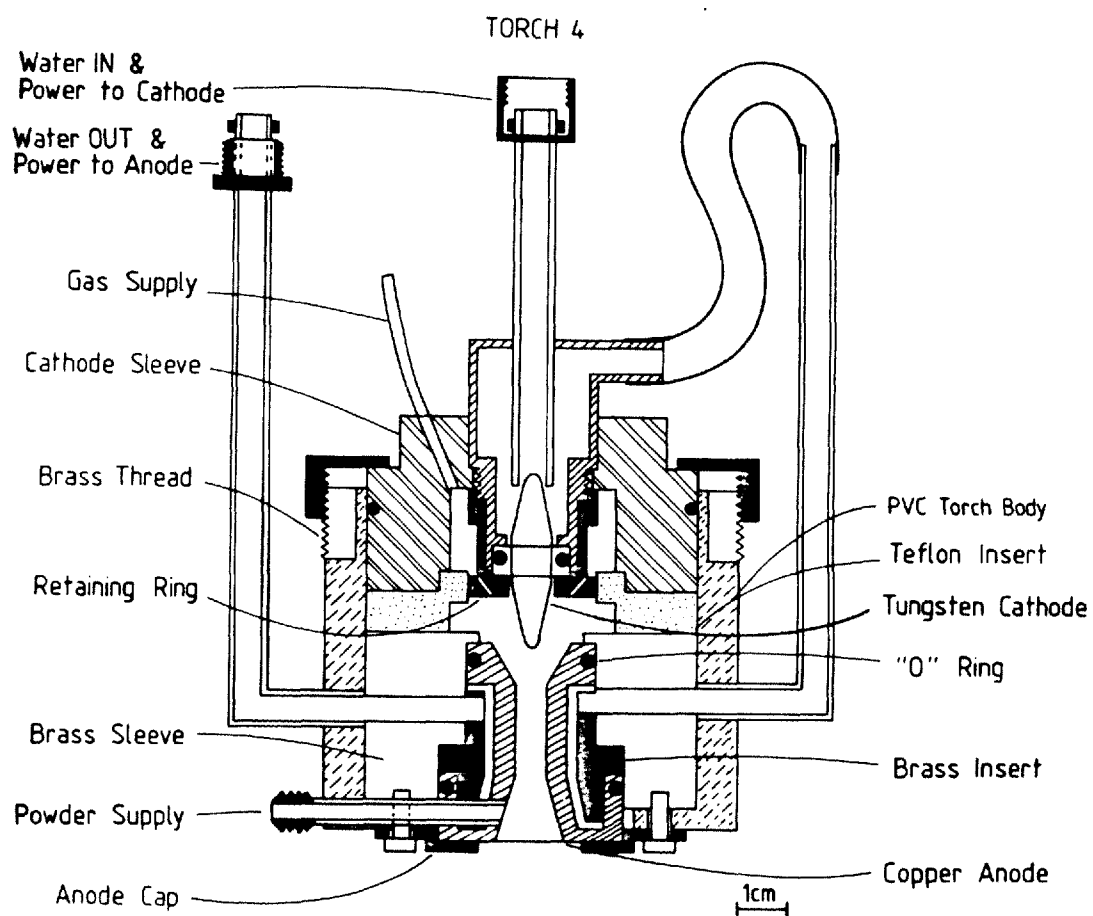


Figure 2.12: Diagram of Torch 4.

in the hot zone of the plasma tail flame. These had internal bore dimensions of,

- (i) 15 mm diameter x 60 mm in length, and
- (ii) 20 mm diameter x 40 mm in length.

The method increased the number of molten particles arriving at the substrate but the coatings revealed defects due to :

- (i) the inclusion of very fine particles which would not under normal conditions have been entrained in the tail flame, and
- (ii) relatively large droplets of molten material which resulted from build up in the anode region and along the walls of the anode extension.

### 2.2.3 Power Supply and Auxillary Equipment

#### 2.2.3.1 Power Supply

The power supply is an integral component of a plasma spraying system and is designed to suit the specific voltage and current characteristics of the torch. The electrical resistance can be found from the elementary relation,

$$R = \frac{V}{I} \quad \dots (2.1)$$

where R = resistance (ohms)

V = voltage (volts)

I = current (amps)

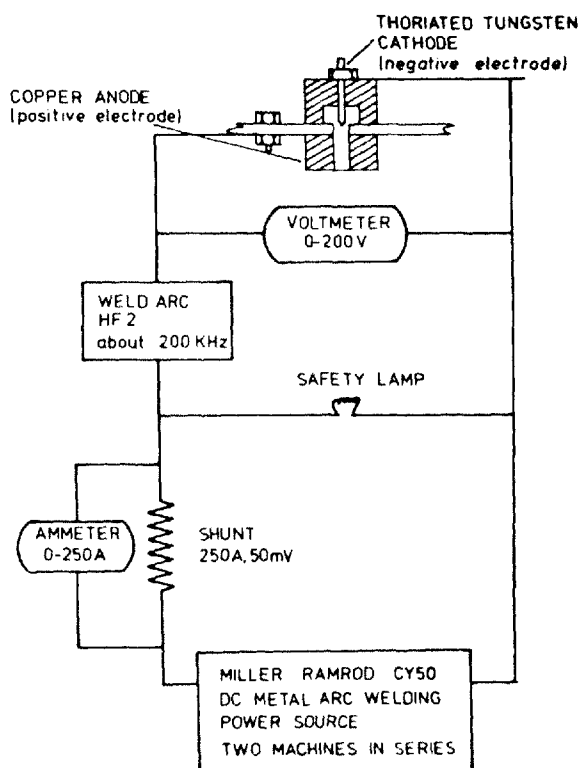
and the electrical power from

$$P = I \times V \quad \dots (2.2)$$

where P = electrical power (watts).

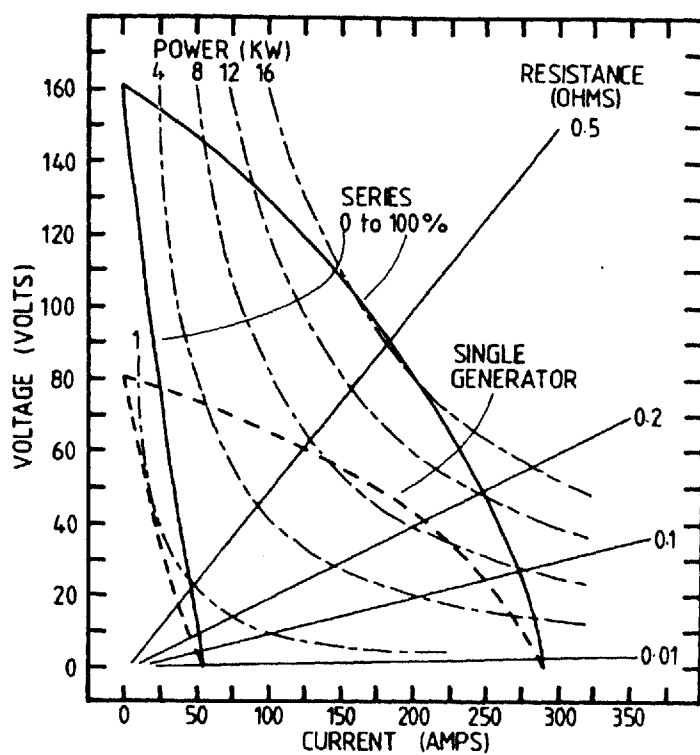
Figure 2.13 shows the voltage-current characteristic curves for two Miller Ramrod CY50 generators (9.1kW power rating each) in either series or parallel combinations. The power and resistance curves have been derived from these. The operating characteristics of the torch lie on these curves with the exact position depending on essentially the anode-cathode distance, the gas type and the gas flow rate.

The high frequency unit (Weld arc HF2) superimposed a 200kHz high voltage current across the anode and cathode during the initial start-up of the torch and permitted the primary ionisation of the arc gas. The original diodes of the generator failed under the high frequency voltage and so these were upgraded according to the changes detailed in Figure 2.14.

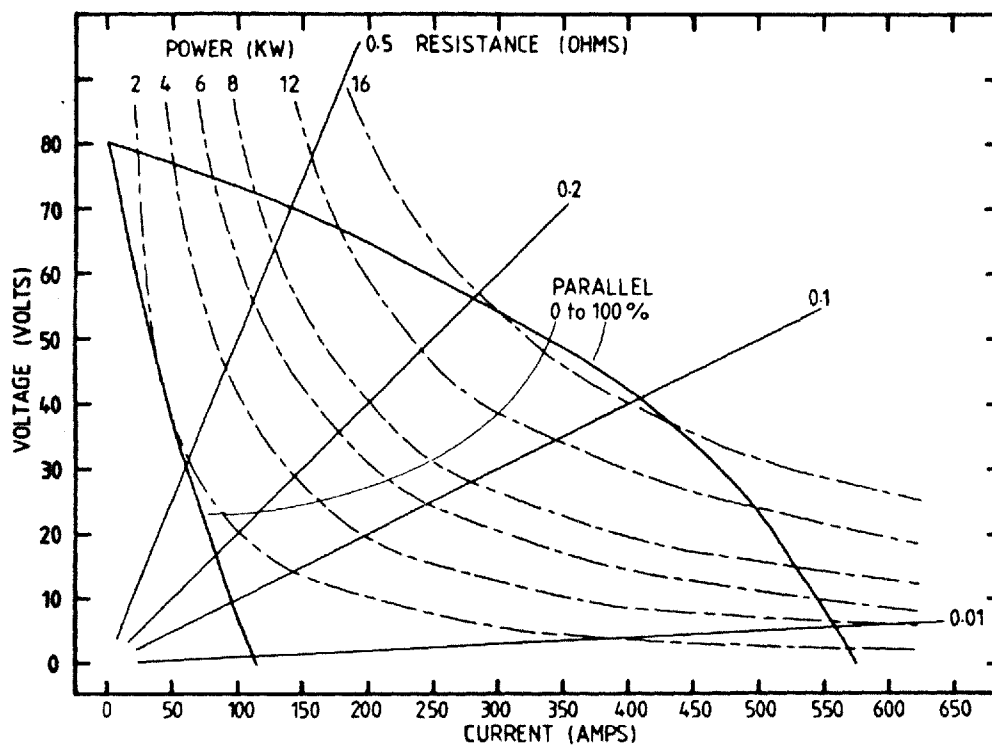


NOTE Modifications to welding sources were  
 (a) Diodes changed (150A 300V to 150A 1000V)  
 (b) Capacitors in parallel with each diode changed (0.01 $\mu$ F at 500V to a series combination of 0.01 $\mu$ F at 1000V and a 10K $\Omega$  10W resistor)  
 (c) Two capacitors in parallel (120pF 3KV and 0.1 $\mu$ F 250V) across the output and input of each supply

Figure 2.14: Electrical circuit of apparatus.



(a)



(b)

Figure 2.13: Voltage-current characteristics of the Miller Ramrod CY50 generators with variable core reactor adjusted from 0 to 100%. Power and resistance curves are superimposed.  
 (a) Generators in series combination.  
 (b) Generators in parallel combination.

Another power supply (CIG. DC 400P) was also used to enable power levels of up to 30 kW (Figure 2.15) to be attained. The first and second power settings where the torch operated with a resistance of 0.1 to 0.5 ohms were most suitable for this work. There are some distinct advantages in having a variable reactor so that the operating voltage and current can be smoothly adjusted and so the series combination of Miller generators were used in parallel with the DC 400P on setting 1 (Figure 2.16).

The high frequency (HF) unit with the larger power supply operated at 500 to 2000 kHz with a voltage of 5 to 20 kV and its operation did not affect the stability of either the DC 400P generator (diodes rated at 300 A and 600 V) or the Miller generators (diodes rated at 150 A and 1000 V).

#### 2.2.3.2 Automatic Control

A semi-automatic control circuit was also obtained from a plasma cutting unit and its slightly modified circuit is shown in Figure 2.17. The features and operation of this unit are described below.

There are a total of 8 relays and solenoids which perform the following control functions:

- (1) ON/OFF switch which starts the plasma system.
- (2) HF start and stop relay.
- (3) A relay to switch the DC generator on and off.
- (4) Water flow rate switch which ensures that sufficient coolant flows through the system.
- (5) A current sensing relay that controls the HF unit and the secondary gas supply.
- (6) A solenoid for secondary gas (normally  $N_2$ ) flow.
- (7) A solenoid to control the water supply.
- (8) A solenoid for primary gas (Ar) flow.

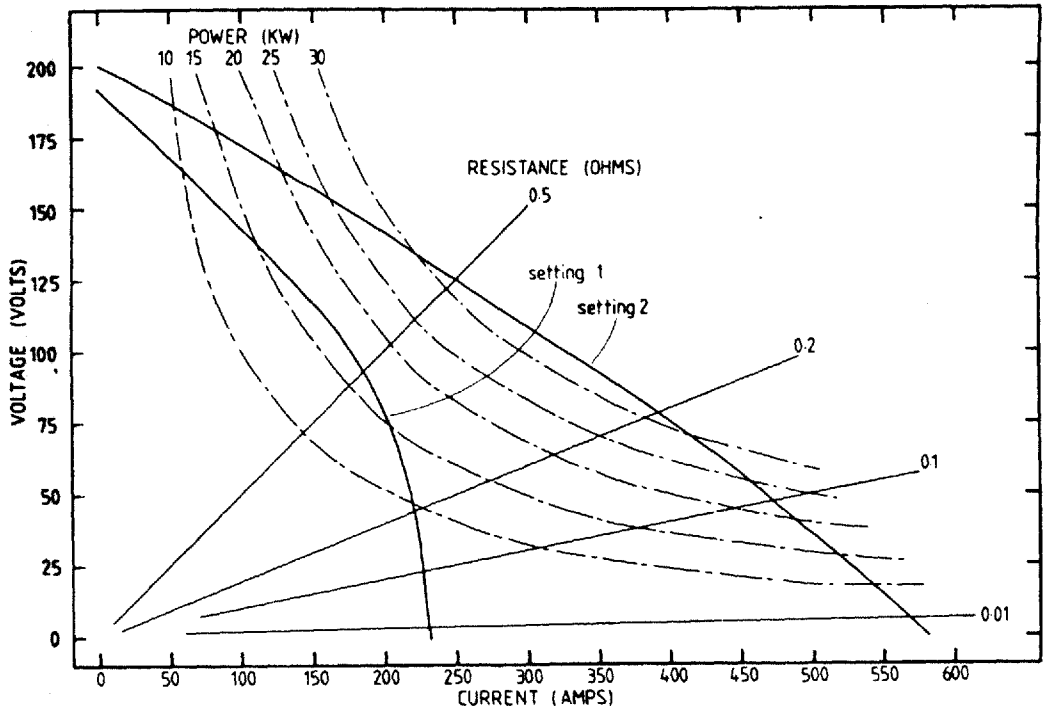


Figure 2.15: Voltage-current characteristics of the CIG DC 400P generator on settings 1 and 2. Power and resistance curves are superimposed.

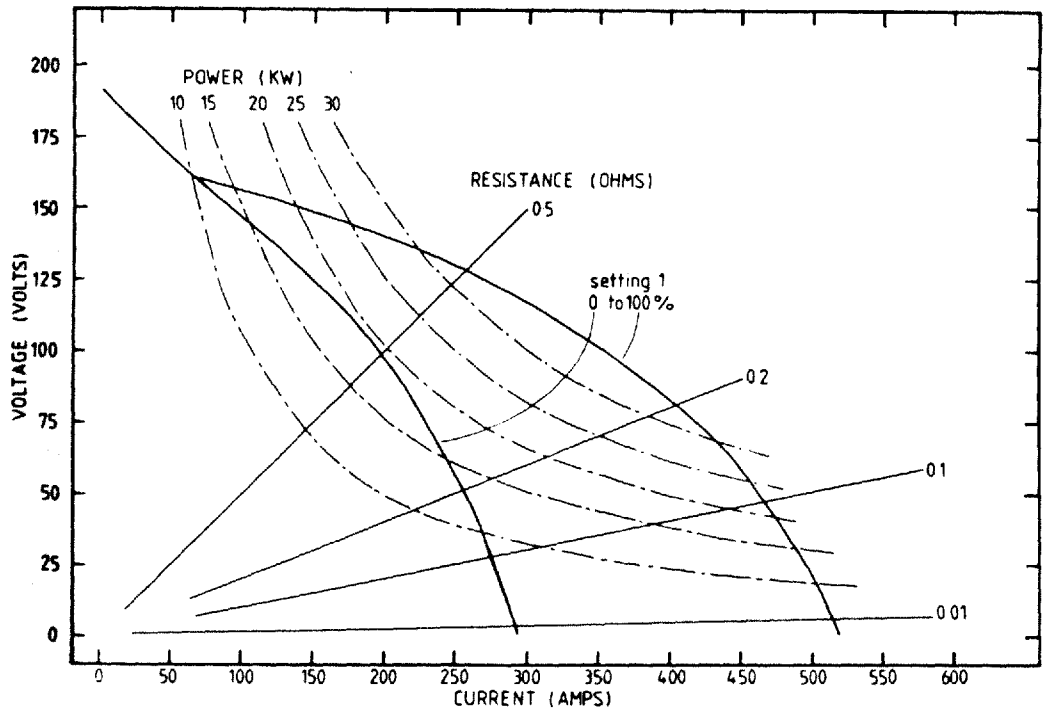


Figure 2.16: Voltage-current characteristics of the CIG DC 400P generator (on setting 1) with the series combination of Miller Ramrod CY50 generators used in parallel (0 to 100% of variable reactor core). Power and resistance curves are superimposed.

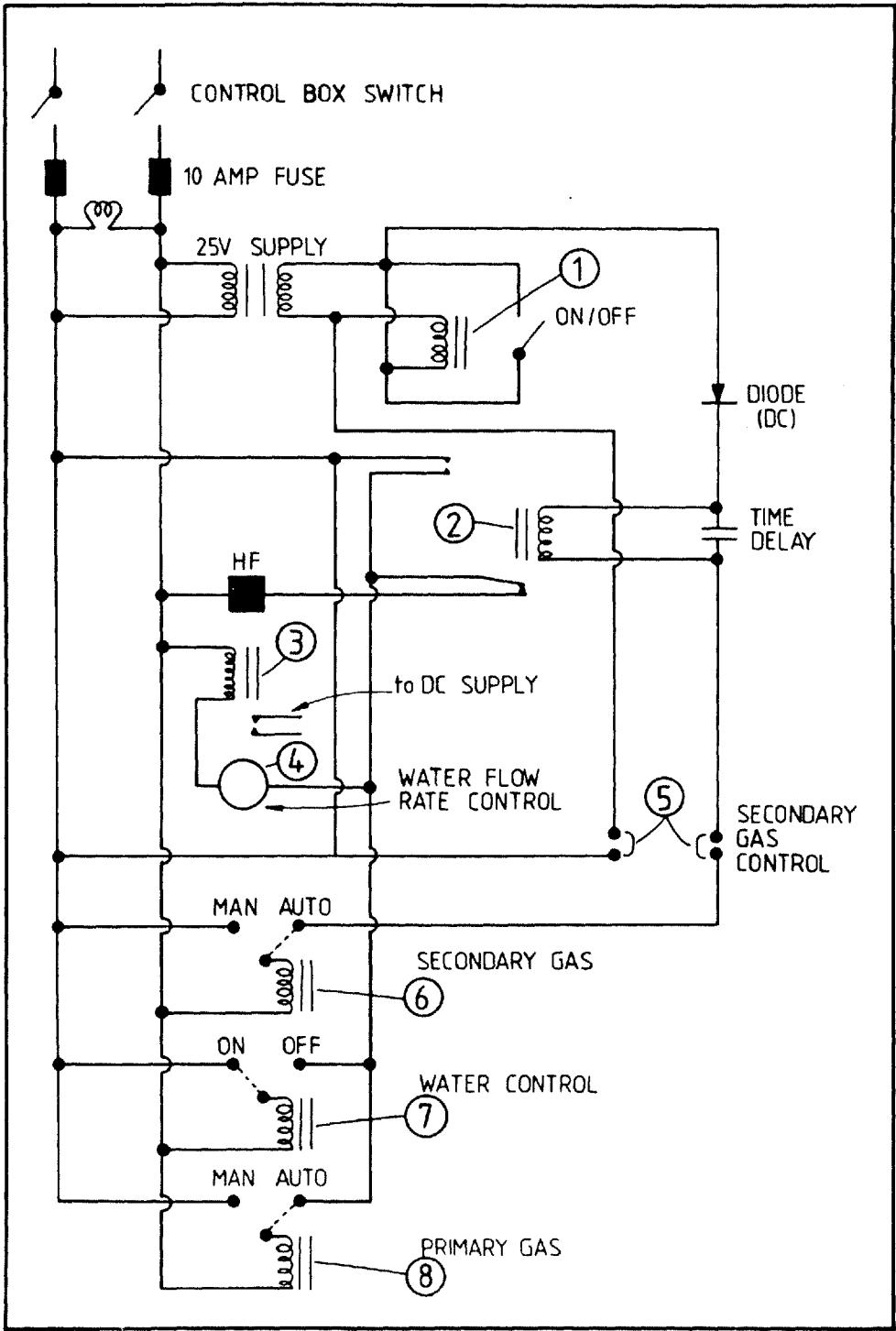


Figure 2.17: Electrical circuit for semi-automatic control unit.

In the stand-by condition, immediately prior to operation, the 2 pole control box switch is closed, relays 1, 3 and 5 are open and relays 2 and 4 are closed. The water flow relay (7) is normally ON while the gas relays (6 and 8) can be set to either manual (MAN) or automatic (AUTO). If set to the manual position then gas flows through the torch prior to relay 1 closing.

If the gas relays are set to the AUTO position then primary arc gas immediately flows through the system when relay 1 is turned ON and at the same time the HF unit operates via relay 2. When relay 1 is closed power is supplied from the generator to the torch via relay 3 only if there is a sufficient water supply to close relay 4. Thus if at any time the water supply is inadequate or interrupted during the torch operation then relay 4 will not close and the power supply will either not come into operation or, if closed, it will turn off. The water switch (relay 7) is only active when relay 1 is open and thus if relay 1 is closed the water cannot be switched off via relay 7 as a means of shutting the system down. Therefore, in summary, when relay 1 is closed the HF unit operates, primary gas flows and the DC circuit to the torch electrodes is closed.

When an electric arc is established between the cathode and anode then the current surge will be detected by relay 5 which then closes. As a result of this relay 2 opens and the HF unit is turned off, and as well relay 6 closes (if in the automatic position) so that the secondary gas flows after a time delay (about 1/10 second) determined by the capacitor. This is the general operating condition of the torch.

The system is closed down by opening relay 1 (i.e. OFF) and the following operation sequence occurs:-

- (i) Relay 3 opens to switch the DC power supply off.
- (ii) Relay 5 opens to switch off the secondary gas supply (if in the AUTO position).
- (iii) Relay 2 closes but the HF does not activate because relay 1

is open. It is not possible for the HF to operate by short circuiting through the primary gas leads (when in the AUTO position) or water supply leads (when in the OFF position).

- (iv) The primary gas is turned off if relay 8 is in the AUTO position whereas if either of the gas controls are in the MAN position they must be switched off (by selecting the automatic position).

#### 2.2.3.3 Cooling System

Many problems associated with the running of a torch can be attributed to a poor water supply which may result in overheating of the anode, cathode or seals. The smallest constriction for the plumbing system is within the torch where cavities are generally the same as the inlet copper tubing - i.e. 6 mm diameter. The pump chosen (Grundfos centrifugal pump No. 2-100) was capable of delivering water at rates up to  $18 \text{ l min}^{-1}$  at  $7.6 \times 10^5 \text{ Pa}$  pressure and this proved adequate.

#### 2.2.3.4 Powder Feeding and Gas Control

The powder feeding unit (Metco Model 3MP) operates on the principle of a rotating slotted wheel which delivers powder from a hopper to a stream of gas (Figure 2.18). The calibration of the variable speed control with respect to wheel rpm and weight of powder is also shown in Figure 2.18.

A gas console was also manufactured and incorporated facilities to control the flow rates of 3 different arc gases. The gas controls were not independent since the flow rate varies with the back pressure and this changes with the total gas flow rate. The flow rate gauges are normally calibrated with air and therefore it

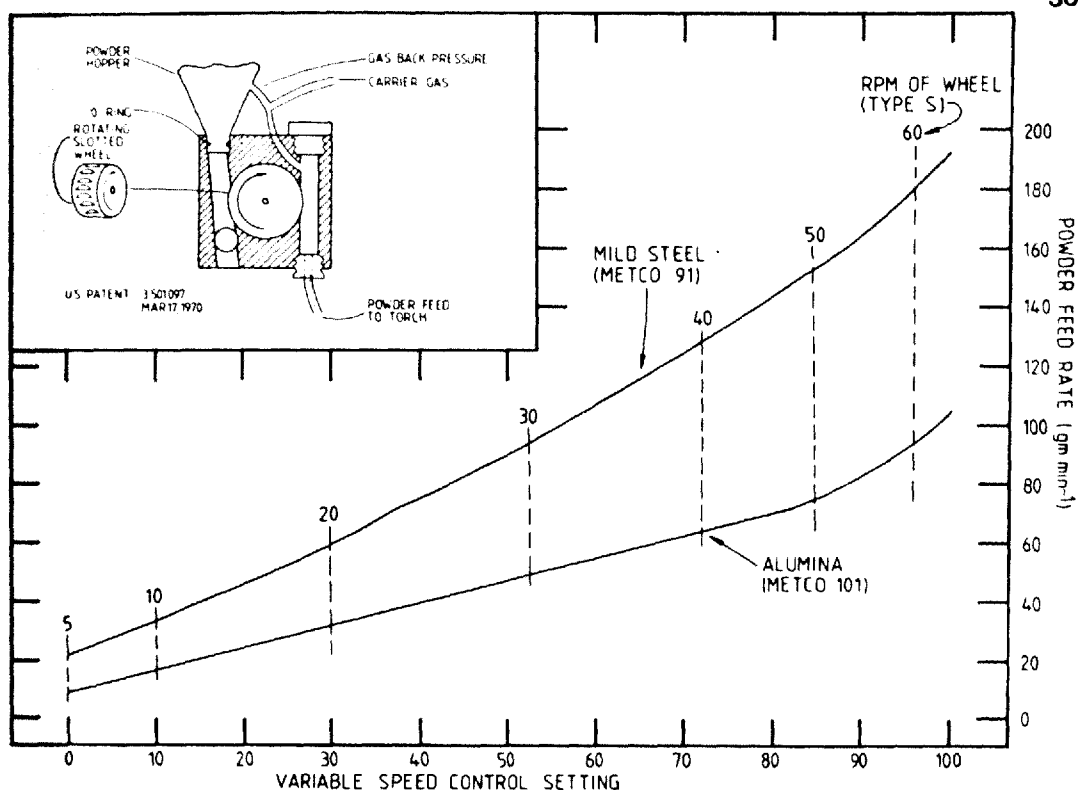


Figure 2.18: Calibration of powder feed (Metco 3MP) variable speed control with respect to delivery rate of powder. Inset shows operating principle of the unit.

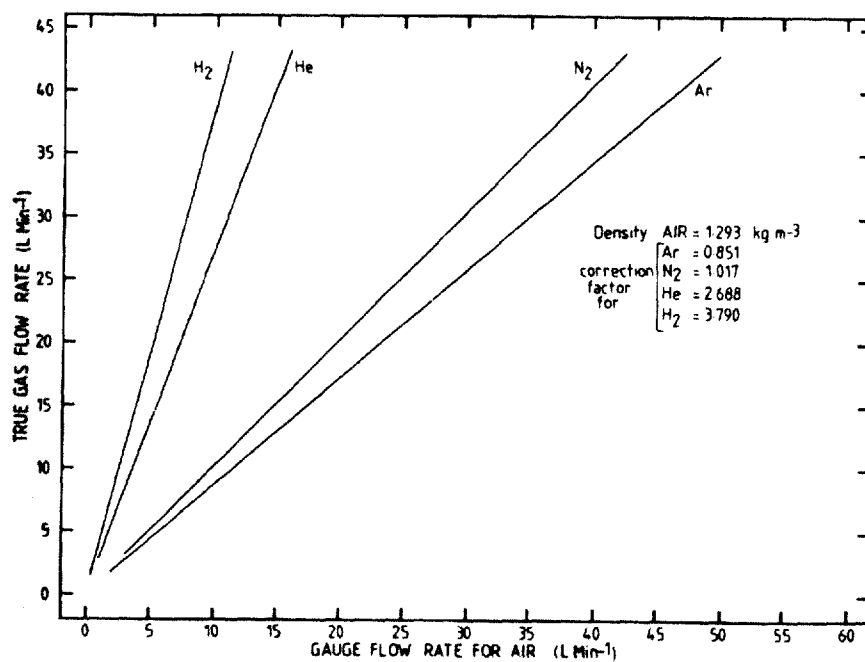


Figure 2.19: Calibration of gas gauges.

is necessary to take into account the gas density by using the equation:

$$f_v = \sqrt{\frac{\text{density of air}}{\text{density of gas}}} \quad \dots (2.3)$$

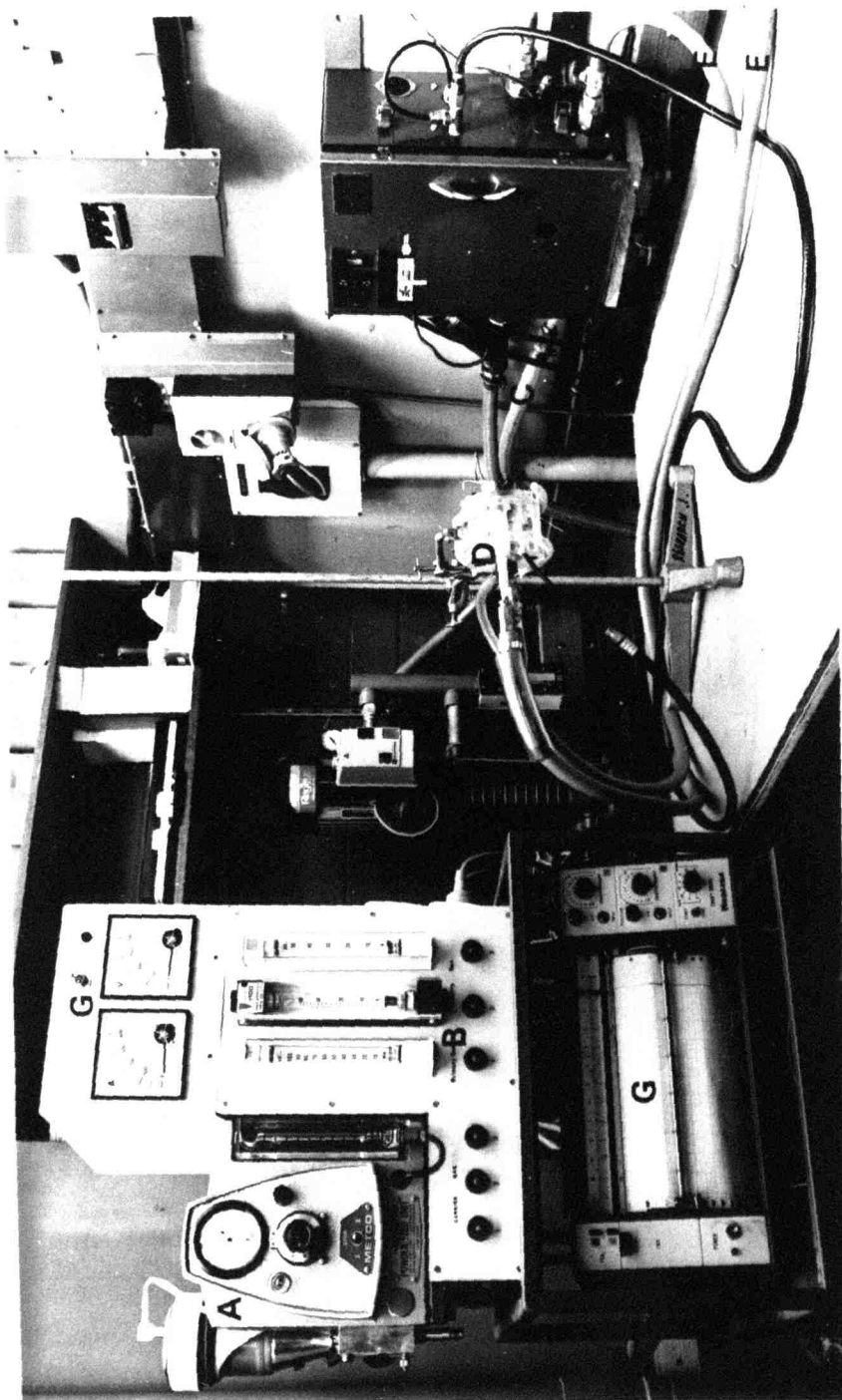
The parameter  $f_v$  is the volumetric correction factor and should be multiplied by the meter reading to establish the true gas flow (Figure 2.19).

The complete plasma spraying system is shown in Figure 2.20 .

#### 2.2.4 Torch Characteristics

The DC400P power supply was used to determine the operating voltage and current of torch 3 with respect to gas type (argon and/or nitrogen), gas flow (20, 25 and 30  $\ell \text{ min}^{-1}$ ) and anode-cathode spacing (1.0 and 4.6 mm). The results (Figure 2.21) follow the same general trend as the characteristics of the generator and any deviations can be mostly attributed to the voltage and current fluctuations of the arc. The voltage fluctuation increased with the mean voltage level and at 85V was a maximum of 12V. The variation of voltage (and current) increases the wear on the anode and cathode so a typical operating voltage of 50 to 60 volts was chosen where the voltage fluctuation is about 5V. At the same time it should be kept in mind that these electrical conditions limit the operating power to low levels of from 12 to 14 kW. During continuous use at these low levels the anode wear is concentrated to the throat region.

The performance characteristics of the generators can also be expressed in terms of power (kW) and resistance ( $\Omega$ ) (Figures 2.22 and 2.23) to indicate the specific voltage and current parameters which can be taken advantage of when using a plasma torch. Maximum



- A) Powder feed unit and powder delivery tube.
- B) Gas control and delivery to torch.
- C) Water supply from pump.
- D) Torch.
- E) Water cooled cables
- F) Control box
- G) Gas, voltage and current recording facilities.

Figure 2.20: Plasma spraying system

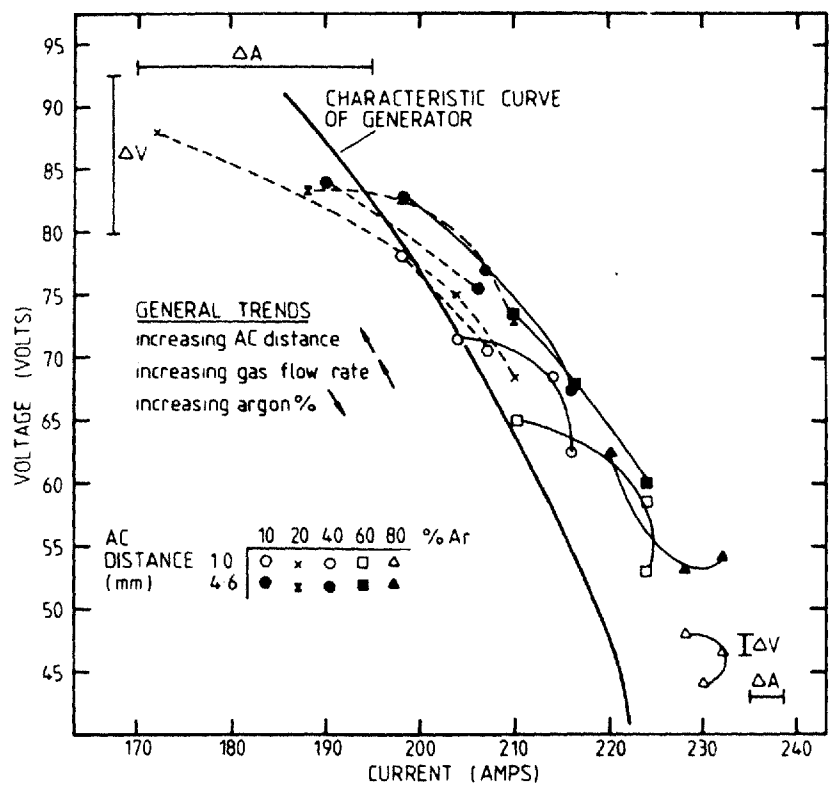


Figure 2.21: Voltage-current characteristics of torch 3.

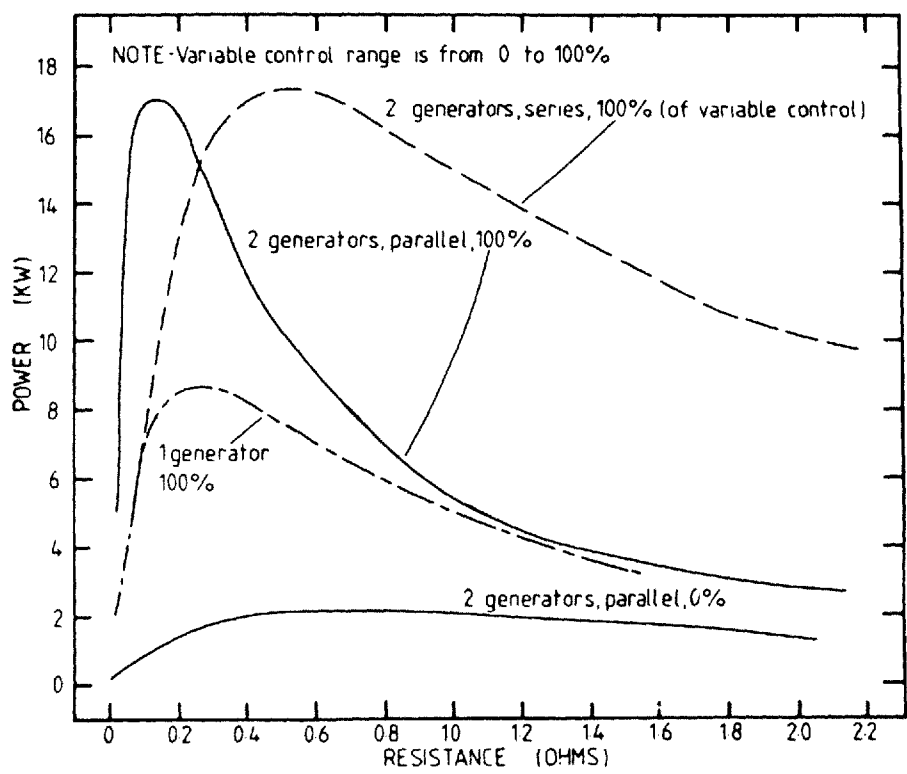
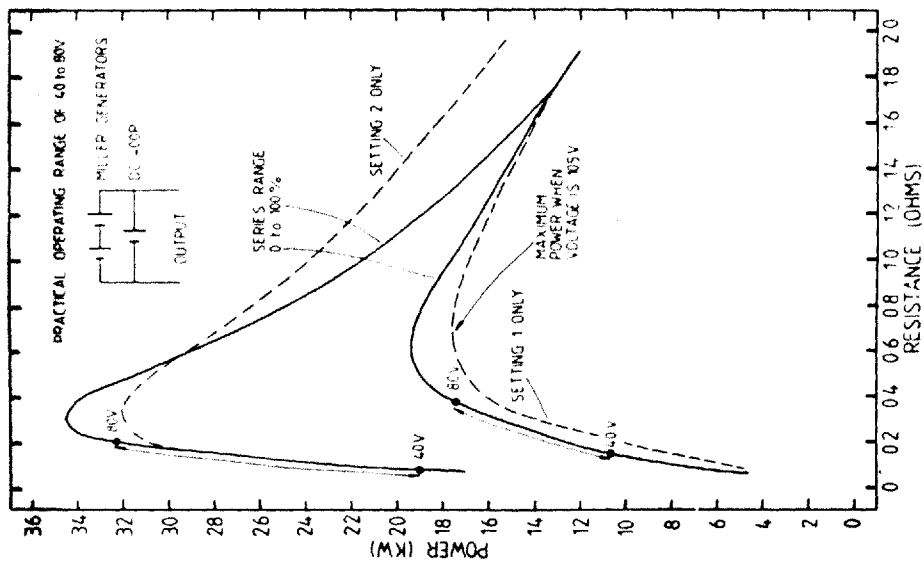
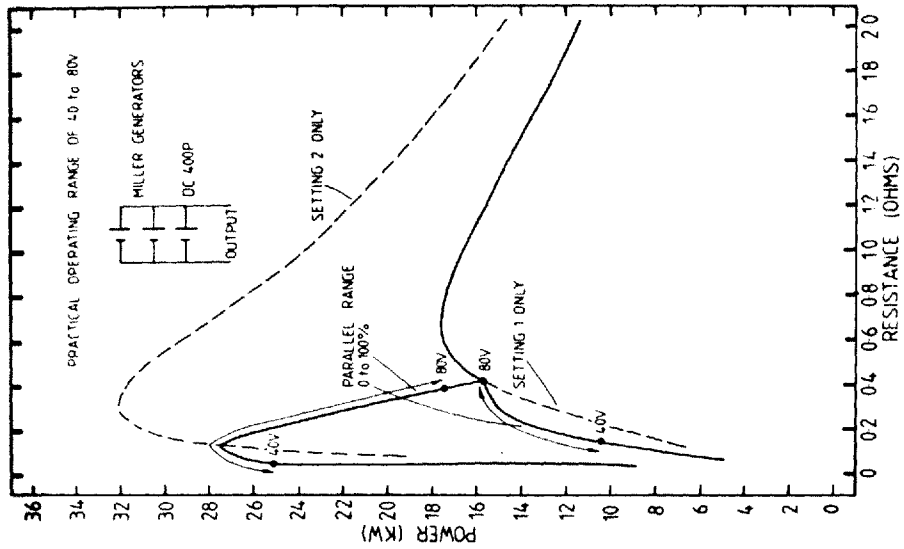


Fig. 2.22: Power-resistance characteristics of the Miller Ramrod CY50 generators in series and parallel combination.



(a) Miller Ramrod Generators in series combination.



(b) Miller Ramrod generators in parallel combination.

Figure 2.23: Power-resistance characteristics of the CIG DC 400P generator (on setting 1) in parallel combination with Miller Ramrod CY50 generators.

power (on setting 1) is obtained at a torch resistance of  $0.6\Omega$  where the voltage is 105V. These operating conditions cannot be reached even when using 100 percent secondary gas mixtures of nitrogen with hydrogen, and as already mentioned the electrode wear rates increase significantly at high voltages. More viable operating conditions (40-80V,  $0.1 - 0.2\Omega$ , 19-30kW) are obtained if setting 2 is used, but the voltage fluctuations are more severe than in the previous case and leads to increased erosion rates of the anode and cathode.

Figure 2.24 shows the current, voltage and power characteristics of the DC400P using torch 3 (replotted from Figure 2.21). The operating voltage generally increases (and therefore the current decreases) with,

- (i) an increase in gas flow rate,
- (ii) more concentrated mixtures of nitrogen in the arc gas, and
- (iii) an increase in the anode-cathode distance.

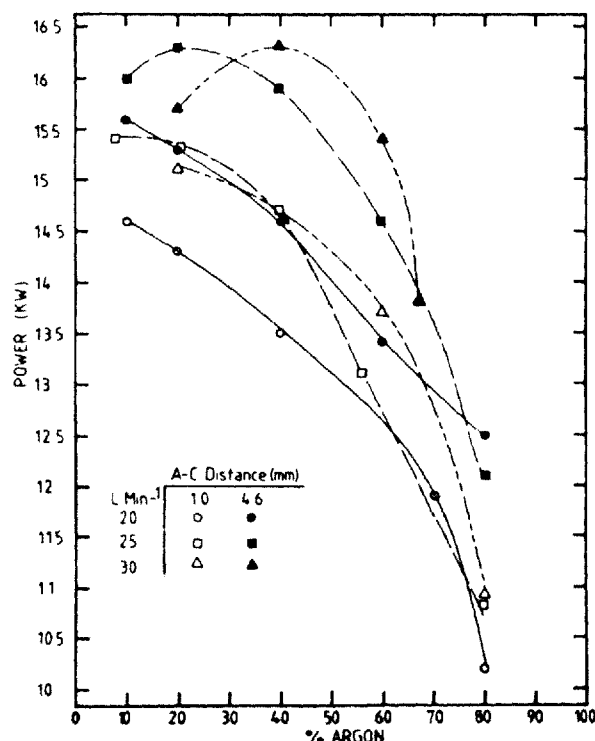


Figure 2.24(a): Characteristics of torch 3. Power - percent argon.

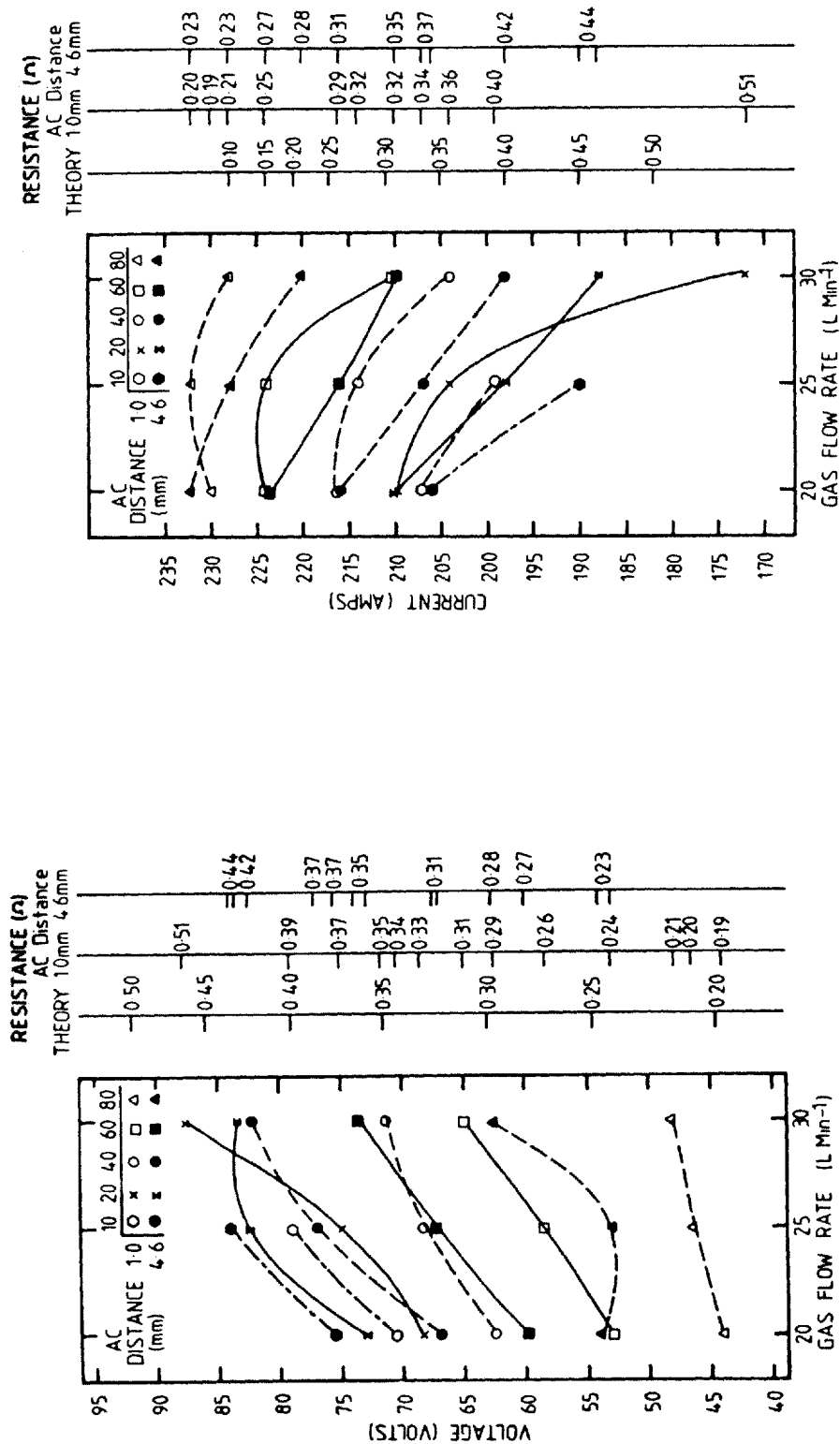


Figure 2.24: Characteristics of torch 3.

The maximum power level (16.3kW) is attained at the large anode-cathode setting (82.5V and 198A) using either a 20% Ar-N<sub>2</sub> mixture flowing at 25  $\ell \text{ min}^{-1}$  or a 40% Ar mixture with a flow rate of 30  $\ell \text{ min}^{-1}$ .

The theoretical resistance (right hand axis of Figures 2.24b and 2.24c) has been calculated with the assumption that the torch operates according to the generator characteristics whereas the experimental resistance has been taken from the running conditions of the torch. These resistance values do not always correlate and the most prominent departure occurs in the current measurement for large anode-cathode settings at high nitrogen concentrations.

Setting 2 of the DC400P generator was used in several trials (Table 2.2a) and the power increase was significant. However the electrodes were observed to erode during use, as shown by bright white sparks or a green flame for the cathode and anode respectively. It was found that direct short circuiting could occur between the electrodes at high power levels (greater than 20 kW) and operating resistances of less than approximately  $0.05\Omega$  and this led to catastrophic failure of the electrodes. These events can be avoided if the operating resistance of the torch is increased to approximately  $0.2\Omega$  by either:-

- (i) adding a suitable secondary gas such as nitrogen,
- (ii) increasing the arc distance between the anode and cathode,
- (iii) increasing the gas flow rate, or
- (iv) choosing a power supply of appropriate electrical characteristics.

Thus the combination of the DC400P in parallel with the series combination of Ramrod generators was used and this permitted relatively high power levels, up to 22 kW (Table 2.2b) to be obtained at torch resistances of approximately 0.1 to  $0.3\Omega$ . The resistance range for torch operation is dependent on the specific arcing characteristics of the gas mixture but generally:



## CHAPTER THREE

## VELOCITY AND TEMPERATURE MEASUREMENTS

## 3.1 NOMENCLATURE

|                 |                                                                               |
|-----------------|-------------------------------------------------------------------------------|
| $C_1$           | - first radiation constant ( $3.7403 \times 10^{-16} \text{ W m}^2$ )         |
| $C_2$           | - second radiation constant ( $1.43879 \times 10^{-2} \text{ m K}$ )          |
| $C_3$           | - third radiation constant ( $2.898 \times 10^{-3} \text{ m K}$ )             |
| $D$             | - absolute density (note that D76 is a trade name)                            |
| $E$             | - exposure ( $\text{ergs cm}^{-2}$ )                                          |
| $f$             | - aperture size of camera                                                     |
| $f(\lambda, T)$ | - function of wavelength and temperature                                      |
| $g$             | - geometrical factor                                                          |
| $I_e$           | - total radiant flux density ( $\text{watts steradian}^{-1}$ )                |
| $l$             | - window-substrate spacing (m)                                                |
| $m$             | - magnification from object to film image                                     |
| $N$             | - revolutions per second ( $\text{sec}^{-1}$ )                                |
| $N_\lambda$     | - spectral radiant exitance ( $\text{W m}^{-2} \text{ nm}^{-1}$ )             |
| $P$             | - displacement of deposit with respect to window (m)                          |
| $Q$             | - Callier coefficient                                                         |
| $R$             | - distance of window from centre of rotation (m) used only in equation (3.1). |
|                 | - response ratio                                                              |
| $T$             | - temperature (K)                                                             |
| $T_{Br}$        | - brightness temperature (K)                                                  |
| $Tr$            | - transmission of filter (percent)                                            |
| $t_{exp}$       | - effective exposure time ( $\text{sec}^{-1}$ )                               |
| $V$             | - particle velocity ( $\text{m sec}^{-1}$ )                                   |

## Greek symbols

|            |                                                                                         |
|------------|-----------------------------------------------------------------------------------------|
| $\epsilon$ | - emissivity                                                                            |
| $\lambda$  | - wavelength (m)                                                                        |
| $\sigma$   | - Stefan-Boltzmann constant ( $5.6697 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ ) |

## Subscripts

|           |                   |
|-----------|-------------------|
| $B$       | - blue            |
| $G$       | - green           |
| $R$       | - red             |
| $max$     | - maximum         |
| $\lambda$ | - wavelength (m)  |
| $T$       | - temperature (K) |

## 3.2 LITERATURE SURVEY

### 3.2.1 Introduction

Velocity and temperature measurements have arisen out of a need for more fundamental knowledge of particle behaviour in a plasma flame in attempts to allow optimisation of the plasma spraying process rather than rely on a completely empirical or "trial and error" approach. In the literature these measurements are included under the term of "plasma diagnostics".

### 3.2.2 Velocity Measurements

Velocity measurements of both the plasma effluent and particles injected into the flame have been carried out. The velocity of flowing gases can be determined from a measurement of the total (stagnation) and local (static) pressures using a pitot tube (Gerdeman and Hecht, 1972, pp. 129-131; Wilkinson and Milner, 1960). These probes are water cooled and can be miniaturised for measuring the velocity at precise locations and thus used to map a cross section of the gas stream.

The velocity of particles in the plasma stream has been determined by a variety of techniques which range from finding an average velocity of a certain size distribution of particles to the velocity of individual particles. The simplest technique (Grisaffe

and Spitzig, 1963; Kharlamov and Ryaboshapko, 1975; Hasui et al., 1965) relies on measuring the horizontal displacement of particles being deposited onto a moving substrate (Figure 3.1). The test coupon, which serves as the substrate, is placed at the required distance from the plasma torch and moved at a high speed. A plate is placed about 1 cm from the substrate surface and shields it from the spray particles, except for a well defined window which creates a shadow for the particles which arrive at the substrate. The relative displacement of this deposit with respect to the window is used in equation (3.1) to find the average velocity of the particles:

$$V = \frac{2\pi RN\ell}{P} \quad \dots (3.1)$$

where  $V$  = average velocity of particles ( $\text{m sec}^{-1}$ )  
 $R$  = distance of window from the centre of rotation (m)  
 $N$  = revolutions per second  
 $\ell$  = distance between window and substrate (m)  
 $P$  = displacement of deposit with respect to window (m).

A major shortcoming is that the measurements are not precise enough to distinguish the velocities of individual particles in a specific region of the plasma. Only the average velocity of many

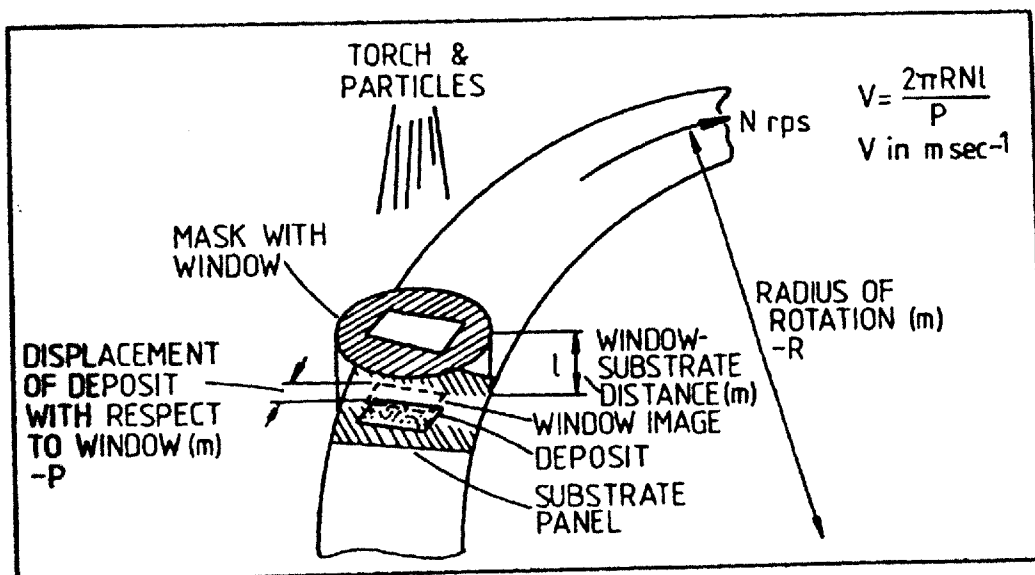


Figure 3.1: Measurement of particle velocity

particles travelling from the window to the substrate is found and this may be very different from the instantaneous velocity on impact with the substrate. On the other hand the technique does not require any special equipment and is simple to perform.

The velocities of individual particles can be found by using high speed photographic processes (Dubovik, 1968). The effective exposure time of a particle moving at a speed of 300 metres per second through a distance of 0.1 to 10 cm is from  $3.3 \times 10^{-5}$  to  $3.3 \times 10^{-3}$  seconds. The upper limit of this range can be obtained with a mechanical shutter. In this case the shutter is made from two curtains which follow each other rapidly across the plane of the film, and effectively form a window which makes one scan of the film. Both the window speed and width may vary (Lemoine et al., 1969) during its scan and Figure 3.2 shows how this may alter the effective exposure time of the film. The window displacement must be perpendicular to the particle movement in order to calculate the particle speed, otherwise the effective exposure time will include a term contributed from the colinear motion of the shutter with respect to the particle direction.

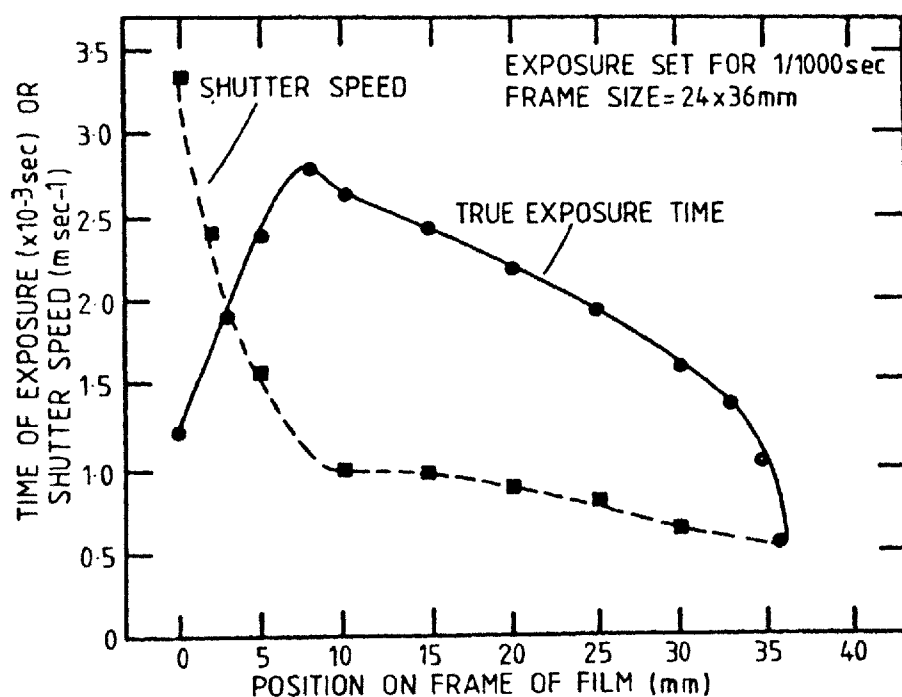


Figure 3.2: Shutter speed and exposure time of a single lens reflex camera with respect to scanning position on film (Lemoine et al., 1969).

More rapid exposures can be made with a high speed cine camera (Lemoine and Le Goff, 1969; Lemoine et al., 1969; Petrov and Morenov, 1967) which typically have maximum film speeds from 36 to 75 metres per second at a frame speed of 33 to 2500 per second (exposure times of  $3 \times 10^{-2}$  to  $4 \times 10^{-4}$  second). Faster exposures giving a time resolution of  $10^{-9}$  second can be obtained with streak cameras (Jordan and King, 1965; Saxe, 1966, pp. 29-43; Dubovik, 1968, pp. 60-82). These cameras use a rotating lens or mirror (revolving at up to  $1920 \times 10^3$  rpm) to sweep the image around an arc of stationary film. The scanning speed determines the resolution of events on the film with respect to time and for these cameras varies from 0.4 to 60 mm per microsecond.

Most recently Barnay et al. (1977) developed a method where the image of particles, as seen by a rapidly vibrating (10 kHz) mirror attached to a speaker cone, was photographically recorded (Figure 3.3). The velocity of the particle with respect to its position in the plasma flame could be calculated from the peak to peak measurements of the recording. This type of analysis would be very complex during the usual operation of a plasma spraying torch since there may be 50,000 particles in the plasma flame at any instant.

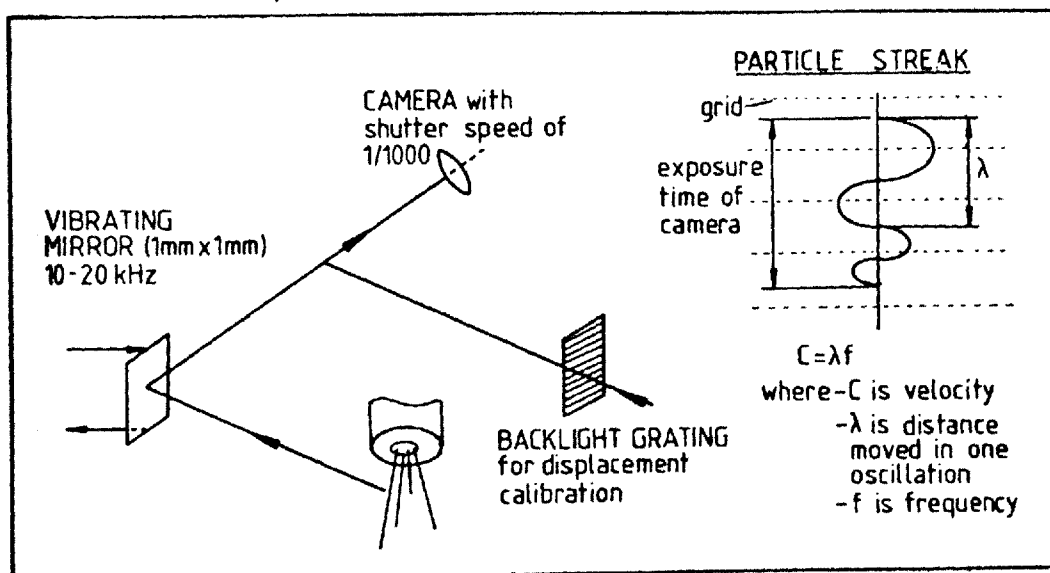


Figure 3.3: Determination of particle speed using a vibrating mirror (Barnay et al., 1977).

Another technique (Fiszdon and Lesinski, 1975; Kruszezka and Lesinski, 1977) measured both the average temperature and velocity of particles simultaneously by analysing the radiation emitted from the particles. A model simulating particles with a particular temperature moving through the plasma flame at different speeds was used to carry out a precise calibration. The radiation of the particle at a specific temperature was simulated by a tungsten lamp with a variable current control. The radiation from the lamp was interrupted twice, first by a screen with a pin hole to represent different particle diameters, and then by a rotating slotted disc (chopper) to simulate various particle velocities. The resultant radiation was detected by a photomultiplier, sensitive to near infra-red wavelengths, and the distribution of the radiation analysed by a multi-channel analyser. Measurements were limited to temperatures greater than  $1900^{\circ}\text{K}$  (for particles about  $50\text{ }\mu\text{m}$  in diameter) because of interference by the radiation emitted from the hot gas surrounding the particles. Another problem was that the emissivity of the test material, alumina, had to be extrapolated into the liquid range which may be unreliable. The data derived from experiments compared satisfactorily to numerical methods that were used to determine the heat transfer and phase change processes of a spherical particle in a plasma jet stream. The numerical method is limited since it did not include the influence of real particle injection conditions which are variable in velocity and particle size distributions.

### 3.2.3 Temperature Measurements

#### 3.2.3.1 Theoretical Considerations

The most direct method of measuring temperature is to deposit the plasma particles onto a thermocouple (Crisaffe and Spitzig, 1963). This does not give a true indication of the particle temperature however since it is difficult to separate the heat contributions from the particles and plasma gas. Also the temperature change of cooling particles is very rapid and the thermocouple response is severely limited by the thermal characteristics of the thermocouple itself. Indirect methods of temperature measurement are based on analysing the radiation emitted by the particles. It is not intended in this work

to present a complete literature survey of the theory and practice behind optical pyrometry (Hinch, 1978) but to provide a summary that is related to the experiments carried out in this work. Definitions of terms which are used in the following text are summarised in Appendix 2 (Meyer-Arendt, 1968; Muray et al., 1971; RCA, 1974, pp. 9-44).

All of the methods are based on the laws of black body radiation. Any body will emit a spectrum of radiation according to Figure 3.4, where the curves represent different temperatures. The total radiance (Hornbeck, 1966) of a black body is related to temperature by the Stefan-Boltzmann law:

$$T = \left( \frac{I_e}{\sigma} \right)^{\frac{1}{4}} \quad \dots (3.2)$$

where  $T$  = temperature (K)

$I_e$  = total radiant flux density (watts per steradian \*)

$\sigma$  = Stefan-Boltzmann constant ( $5.6697 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ )

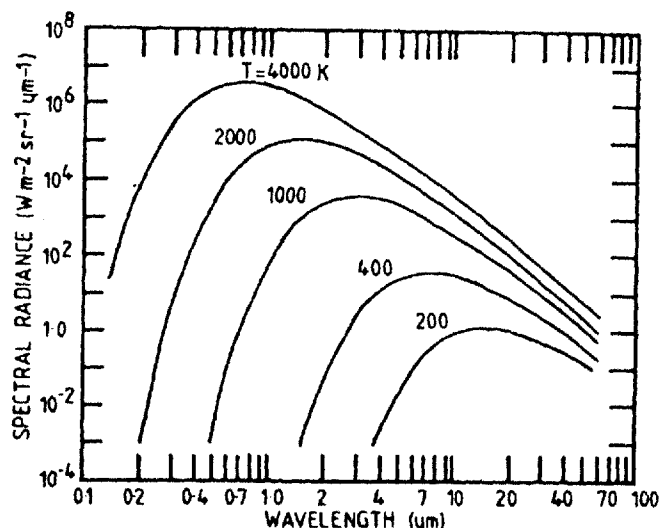


Figure 3.4: Black body spectral radiance as determined by the Planck equation.

\*

The subscript "e" refers to the radiometric quantity and  $I_e$  is meaningful over the entire electromagnetic spectrum.

$I_v$  is the photometric equivalent and is used over the visible portion of the spectrum ( $380 < \text{wavelength} < 770 \text{ nm}$ ). The subscript "c" is used here to distinguish the total radiant flux density from the term  $I$  which is used to represent the electrical quantity of current.

The radiance at any wavelength (the spectral radiance) can be related to the wavelength and temperature by the Planck radiation equation:-

$$N_{\lambda} = C_1 \lambda^{-5} \epsilon g \left[ \exp \left( \frac{C_2}{\lambda T} \right) - 1 \right]^{-1} \quad \dots (3.3)$$

where  $N_{\lambda}$  = spectral radiant exitance ( $\text{W m}^{-2} \text{ nm}^{-1}$ )  
 $\lambda$  = wavelength (m)  
 $T$  = temperature (K)  
 $C_1$  = constant term ( $3.7403 \times 10^{-16} \text{ W m}^2$ )  
 $C_2$  = constant term ( $1.43879 \times 10^{-2} \text{ m K}$ )  
 $\epsilon$  = emissivity (dimensionless)  
 $g$  = geometrical factor.

The term  $\epsilon$  generalises the expression to include non-black body emitters where the emissivity is not 1 while the term  $g$  shows that the geometry of the emitting body must be carefully defined. This equation forms the basis of finding the brightness temperature in the disappearing filament pyrometer (Lovejoy, 1962; Dyne and Penner, 1953). Thus a selected bandwidth of radiation from the source is compared (visually) to filtered radiation from a tungsten filament. The filament current is varied until the filament appears to have the same brightness as the source and the temperature is read directly from the instrument. Equation (3.3) can be corrected (Dyne and Penner, 1953) for the emissivity of the source by:-

$$\frac{1}{T} - \frac{1}{T_{\text{Br}}} = \frac{\lambda}{C_2} (\ln \epsilon_{\lambda}) \quad \dots (3.4)$$

where  $T$  = temperature of filament (K)  
 $T_{\text{Br}}$  = brightness temperature (K)  
 $\lambda$  = wavelength (m)\*  
 $C_2$  = constant ( $1.43879 \times 10^{-2} \text{ m K}$ )

continued....

---

\* Usually the wavelength of a pyrometer is taken as the average wave length of the transmitted radiation.

where  $\epsilon_{\lambda}$  = average emissivity of source over the wavelength response region of the pyrometer.

The geometrical factor of equation (3.3) can be eliminated if two wavelengths from the source are examined. Planck's law is used to find the ratio of the spectral radiation at both wavelengths (Hornbeck, 1966). For a non-black body at a temperature T:-

$$\left. \begin{array}{l} \text{at wavelength } \lambda_1 \\ N_{\lambda_1} = f(\lambda_1, T) \epsilon_{\lambda_1} g \\ \text{at wavelength } \lambda_2 \\ N_{\lambda_2} = f(\lambda_2, T) \epsilon_{\lambda_2} g \end{array} \right\} \dots (3.5a)$$

where  $f(\lambda, T)$  represents the Planck law at an average wavelength. The response ratio (R) defines the colour temperature.

$$R = \frac{N_{\lambda_1}}{N_{\lambda_2}} = \frac{f(\lambda_1, T)}{f(\lambda_2, T)} \frac{\epsilon_{\lambda_1}}{\epsilon_{\lambda_2}} \dots (3.5b)$$

The filters used to analyse the radiation may have a broad wavelength of transmission and Herne (1953) has modified equation (3.5b) to account for the variation of emissivity with wavelength. The two colour temperature measurement is more sensitive for two wavelengths that have a wide separation.

The temperature can also be defined as the wavelength for maximum spectral radiance according to the Wien displacement law:-

$$T = \frac{C_3}{\lambda_{\max}} \dots (3.6)$$

where T = temperature (K)

$C_3$  = constant ( $2.898 \times 10^{-3}$  m K)

$\lambda_{\max}$  = wavelength of maximum spectral radiance (m)

The experimental section of the present work (section 3.3) is concerned with determinations of particle temperature by the two colour method and employs Planck's law to find the response ratio via an equation of the form (3.5b). It should be possible, in principle, to determine the temperature of a particle within the plasma jet as a function of distance from the torch nozzle using two streak photographs taken through different filters. The temperature could be determined from the response ratio and, knowing the particle temperature, its velocity could be determined from the radiant intensity. This sort of result, where the velocity and temperature of individual plasma sprayed particles are found as a function of distance from the torch nozzle, would provide useful data in study of the heat transfer to particles in plasma gases. This data is not available from measurements which give means and distributions for large numbers of particles.

### 3.2.3.2 Experimental Details

Various sensing devices have been used to monitor the spectral radiance of a body. As mentioned previously some investigators (Fiszdon and Lesinski, 1975; Kruszezwska and Lesinski, 1977; Fiszdon, 1979) have used a photo-multiplier to measure intensity over the infra-red region of the spectrum and compared the particle size, temperature and velocity to that of a tungsten filament which has been calibrated. Photographic methods have been used extensively in the field of combustion research under the term "photothermography". As the term suggests the sensing medium is photographic film where the degree of blackening or exposure of the film can be related to the "brightness temperature" of the source (Beral, 1949). Infra-red films are suitable for temperature measurements in the range of 160 to 500°C (Beral, 1949), and in some cases 20 to 950°C (Chion, 1956), whereas at higher temperatures panchromatic film (sensitive to visible radiation) can be used.

Male (1951) used Eastman Super XX panchromatic film in conjunction with a Wrattan 29 filter (transmits radiation of wavelength

greater than 600 nm) to analyse the radiation of wavelength 600 to 650 nm emitted from a ram jet combustion chamber. The images of four tungsten ribbon lamps at different temperatures were recorded simultaneously with the test target to allow calibration of the film. Temperatures of up to 1800°K were recorded in this way using shutter speeds of 1/45 second at a lens aperture of f32.

Tyroler (1956) modified this technique to record explosive phenomena at rates of 2000 frames per second. A similar calibration method was used where three standard temperature sources were superimposed onto the film with the event, and brightness temperatures up to 2700°K could be measured. For measurements at higher temperatures the film exposure can be attenuated by placing a filter of known transmission of the appropriate wavelength (600 to 640 nm) in front of the camera lens. In this case the film exposure for the reference temperatures are not attenuated and the temperature of the event can be calculated from the equation:-

$$C_1 \lambda^{-5} e^{-C_2/\lambda T_{Br}} = Tr C_1 \lambda^{-5} e^{-C_2/\lambda T} \quad \dots (3.7a)$$

where  $C_1$ ,  $\lambda$ ,  $C_2$ ,  $T$  are the same as in equation (3.3)

$Tr$  = percent transmission of the neutral filter

or

$$T = \frac{C_2 T_{Br}}{(T_{Br} \lambda \ln Tr + C_2)} \quad \dots (3.7b)$$

The accuracy of the method is reported to be 10.0 °K in a range of 2800 °K.

An extensive investigation using the photothermographic technique was carried out by Neurath and Gibbs (1963) in examining the temperature decay and arc processes of a cathode in a DC plasma torch. A 16 mm high speed (5000 frames per second) cinecamera recorded

the processes occurring at the cathode tip, upon arc extinction, through a 650 nm narrow band interference filter. A tungsten filament simulated a range of temperatures for a variety of camera conditions and allowed the film exposure to be correlated for the true film speed, the camera lens aperture and the emissivity of the cathode spot. Twenty to a few hundred frames of the film were analysed by microdensitometry and a cooling curve of the tungsten tip constructed. It was found that the cathode ran at approximately  $2893^{\circ}\text{K}$  when using helium as the working gas compared to  $2753^{\circ}\text{K}$  for argon.

The principles of photothermography are well known and essentially rely on exposing film to radiation from the event and at the same time establishing some empirical calibration from a well defined source, normally tungsten ribbon. The most suitable camera conditions (aperture and shutter speed) to expose the film are found by experiment, and the density measured by a microdensitometer. The radiation from the event is filtered to pass a well defined wavelength and Planck's law can be applied to find the brightness temperature. The advantage of the optical pyrometric method is that the measurement doesn't influence the event as in the case of a thermocouple and, the additional advantage of the photothermographic technique is that, temperature may be permanently recorded with respect to both time and displacement. On the other hand, at its present stage of development, the method is very labour intensive.

### 3.3 PHOTOTHERMOGRAPHY OF PARTICLES IN A PLASMA JET

#### 3.3.1 Calibration of Film

##### 3.3.1.1 Introduction

The previous section has shown that photographic methods have already been extensively used to determine high temperatures. Essentially these techniques involve comparing the film density, after exposure to the source at some unknown temperature, to a standard which is usually a tungsten filament. The resolution of this technique can be considerably enhanced if two radiation bands from the source are examined simultaneously and this is termed "two colour pyrometry". Thus the ratio of film density through two radiation bands is used as a means of measuring temperature. The major advantage of the two colour method is that the response ratio expression eliminates the requirement to know the particle emissivity (see expression 3.5b) if it is assumed that

$$\epsilon(\lambda_1, T) \doteq \epsilon(\lambda_2, T) \quad \dots (3.8)$$

Also if this process is carried out photographically then many particles can be analysed simultaneously and the relationship of temperature with distance from the torch examined.

The two colour method described above seemed worthy of examination because the streak density, as observed during routine photography of the experimental apparatus, varied from particle to particle and with distance of the particle from the torch. However on a critical examination of the experimental data there were several shortcomings that prevented a simple, one to one, correspondence of response ratio to temperature. Therefore it is necessary to correlate Planck's law directly to the film density and this procedure entails following the principles of sensitometry and various correction factors to the film exposure.

The following sections detail experiments carried out:

- (i) to verify that the practical density of film development follows the known theory, and
- (ii) to analyse particles in the tail flame of a plasma.

### 3.3.1.2 Film Exposure and Density Measurements

Various 35 mm films and development procedures (Table 3.1) were used to photograph the torch jet during plasma spraying of mild steel powder and the negatives inspected to choose the most suitable schedule. In these studies the whole emission spectrum from the source was used to expose the film whereas subsequent work incorporated various filters so that only a specific range of wavelengths (blue, green or red) exposed the film.

Table 3.1: Processing Schedules of Film (Temperature = 20°C)  
(Chemicals and film are ex Kodak)

| Film           | Developer  | Dilution | Development Time (min) |
|----------------|------------|----------|------------------------|
| Orthochromatic | D19        | 1:2      | 3                      |
| "              | D19        | N11      | 4                      |
| "              | DK50       | 1:1      | 6                      |
| "              | DK50       | 1:1      | 10                     |
| "              | Microdol X | N11      | 14                     |
| "              | D8         | 1:2      | 3                      |
| "              | D8         | N11      | 3                      |
| Tri-X          | Microdol X | N11      | 14½                    |
| "              | D19        | 1:1      | 4                      |
| "              | D76        | N11      | 11½                    |
| "              | D76        | N11      | 16                     |

It was established that the most suitable 35 mm film was Kodak Tri-X (ASA speed rating of 400) which was developed in undiluted D76 (at 20°C for 16 min.) and this schedule was adhered to in the following trials.

The temperature calibration of the film was carried out by photographing (Pentax spotmatic camera, 135 mm focal length - f3.5 macrolens with a bellows extension tube) the tungsten filament of a diode (Ferranti guard ring diode, type GRD7) at various temperatures which could be obtained by varying the current (Figure 3.5). The film

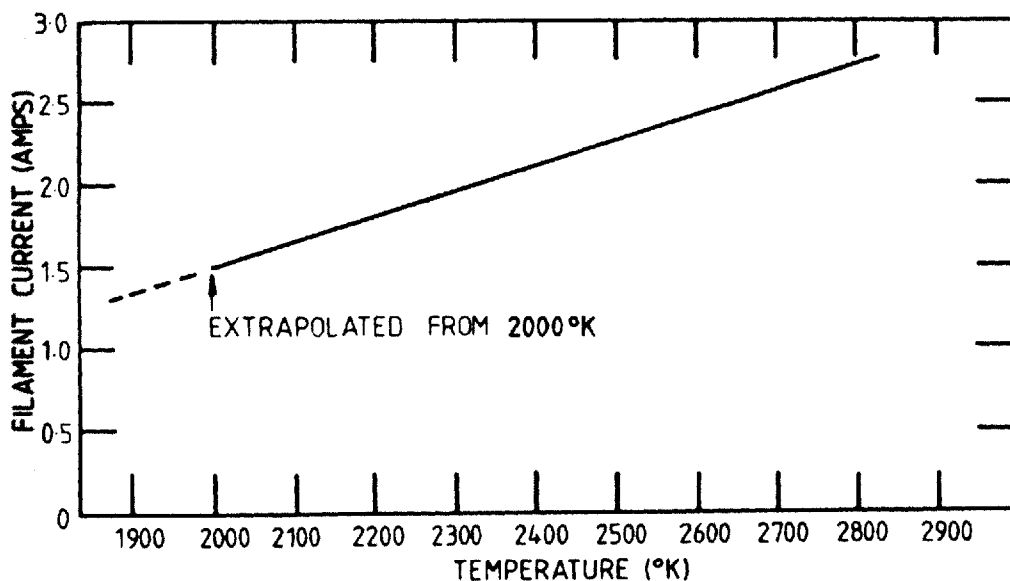


Figure 3.5: Temperature calibration of GRD7 diode with respect to filament current.

was exposed at various camera settings (shutter speeds of  $1/1000$  and  $1/500$  sec, f stop of 3.5, 5.6 and 8) through blue and green filters (Kodak Wratten gelatin filters No. 98 and 99 respectively) for temperatures ranging from 1900 - 2600°K. The film was developed according to the standard conditions and the density of the filament images (Table 3.2) measured with a Joyce automatic microdensitometer (model MK 111C).

Table 3.2: Density Measurements of Film \*

| F3.5 at 1/1000 sec. |                    |                     |                          | F5.6 at 1/500 sec. |                    |                     |                       |
|---------------------|--------------------|---------------------|--------------------------|--------------------|--------------------|---------------------|-----------------------|
| Temp.<br>°K         | Blue(B)<br>density | Green(G)<br>density | B/G<br>response<br>ratio | Temp.<br>°K        | Blue(B)<br>density | Green(G)<br>density | B/G response<br>ratio |
| 1920                | 0.66               | 1.58                | 0.42                     | 1920               | 0.60               | 1.17                | 0.51                  |
| 2000                | 1.38               | 2.05                | 0.67                     | 2000               | 1.27               | 1.99                | 0.64                  |
| 2160                | 1.88               | 2.46                | 0.76                     | 2075               | 1.70               | 2.42                | 0.70                  |
| 2325                | 2.41               | 2.85                | 0.85                     | 2160               | 2.20               | 2.74                | 0.80                  |
| 2500                | 2.89               | 3.19                | 0.91                     | 2250               | 2.45               | 2.92                | 0.84                  |
| 2665                | 3.16               | 3.23                | 0.98                     | 2325               | 2.72               | 3.02                | 0.90                  |
|                     |                    |                     |                          | 2500               | 3.00               | 3.30                | 0.91                  |
|                     |                    |                     |                          | 2665               | 3.22               | 3.40                | 0.95                  |

| F5.6 at 1/1000 sec. |                    |                     |                          | F8.0 at 1/1000 sec. |                    |                     |                       |
|---------------------|--------------------|---------------------|--------------------------|---------------------|--------------------|---------------------|-----------------------|
| Temp.<br>°K         | Blue(B)<br>density | Green(G)<br>density | B/G<br>response<br>ratio | Temp.<br>°K         | Blue(B)<br>density | Green(G)<br>density | B/G response<br>ratio |
| 1920                | 0.31               | 0.68                | 0.46                     | 1920                | 0.28               | 0.41                | 0.68                  |
| 2000                | 0.58               | 1.03                | 0.56                     | 2000                | 0.34               | 0.68                | 0.50                  |
| 2075                | 0.94               | 1.37                | 0.69                     | 2075                | 0.67               | 1.16                | 0.58                  |
| 2160                | 1.14               | 1.58                | 0.72                     | 2160                | 0.97               | 1.32                | 0.73                  |
| 2250                | 1.34               | 1.78                | 0.75                     | 2250                | 1.42               | 1.94                | 0.73                  |
| 2325                | 1.70               | 2.04                | 0.83                     | 2325                | 1.74               | 2.23                | 0.78                  |
| 2500                | 1.91               | 2.26                | 0.85                     | 2500                | 2.10               | 2.53                | 0.83                  |
| 2665                | 2.36               | 2.77                | 0.85                     | 2665                | 2.77               | 2.89                | 0.96                  |

\* Absolute density measured (includes measurement of the fog level)

The response ratio is defined as -

$$R_{(B/G)} = \frac{\text{Density of image through blue filter}}{\text{Density of image through green filter}} \quad \dots (3.9)$$

and can be used as an indication of the filament temperature (Figure 3.6, Table 3.2). At a specified temperature the response ratio increases with an increase in the expose time and this is brought about by:

- (i) increasing the shutter duration (i.e. from  $1/1000$  to  $1/500$  sec.).
- (ii) increasing the aperture size (i.e. decreasing the f stop).

### 3.3.1.3 Theoretical Calculations

The response ratio can be calculated on the basis of the Planck law (equation 3.3) if the following factors are taken into consideration (Figure 3.7):

- (1) Tungsten is not a black body radiator and its emissivity depends on both the temperature and the specific wavelength being examined, Figure 3.8, (Weast, 1974). The emissivity can also be determined from the equation :

$$\epsilon(\lambda, T) = 1.387 \times \lambda^{-0.18} + \left\{ (0.005 + (1.25 \times 10^{-5} \lambda)) \times \left( \frac{2200 - T}{600} \right) \right\} \dots (3.10)$$

where  $\lambda$  = wavelength (nm)

T = temperature (K)

- (2) The radiation is further attenuated on passing through filters (Figure 3.9).
- (3) The effective f stop when using the bellows can be found from the expression (Arnold et al., 1971, p. 155)

$$f(\text{effective}) = (1 + m)f \dots (3.11)$$

where  $m$  = the magnification (from object to film image)

$f$  = the aperture size according to the lens calibration.

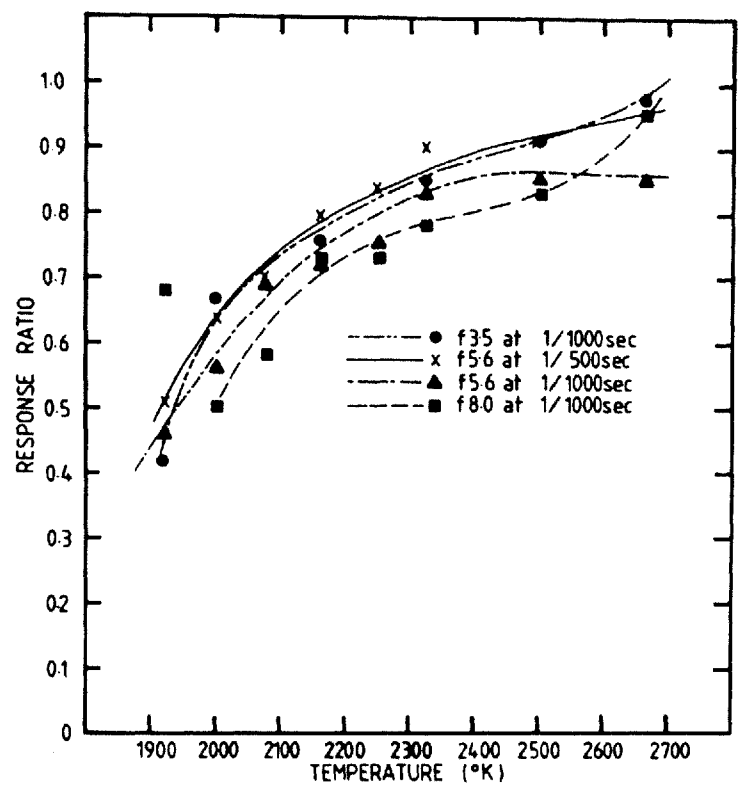


Figure 3.6: Response ratio (Blue/Green) of temperature source at various camera settings.

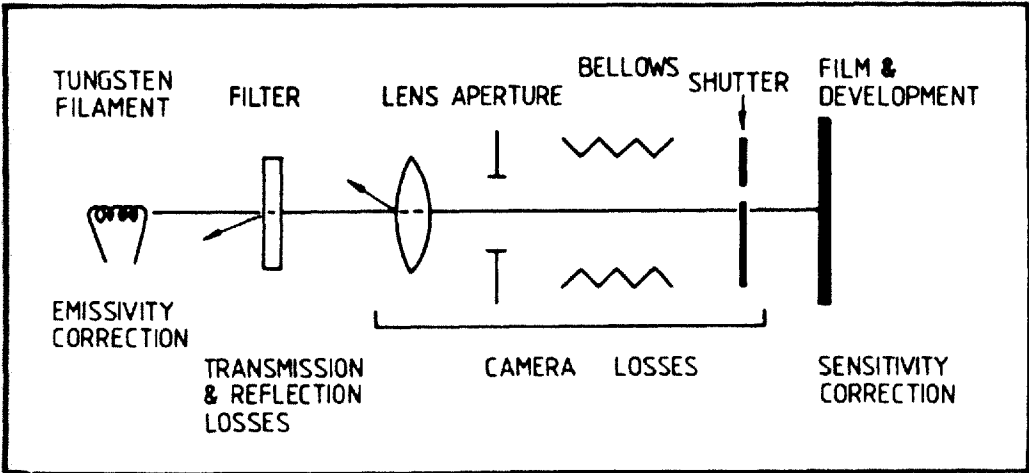


Figure 3.7: Factors to be taken into account when calculating the total transmitted radiance of a source.

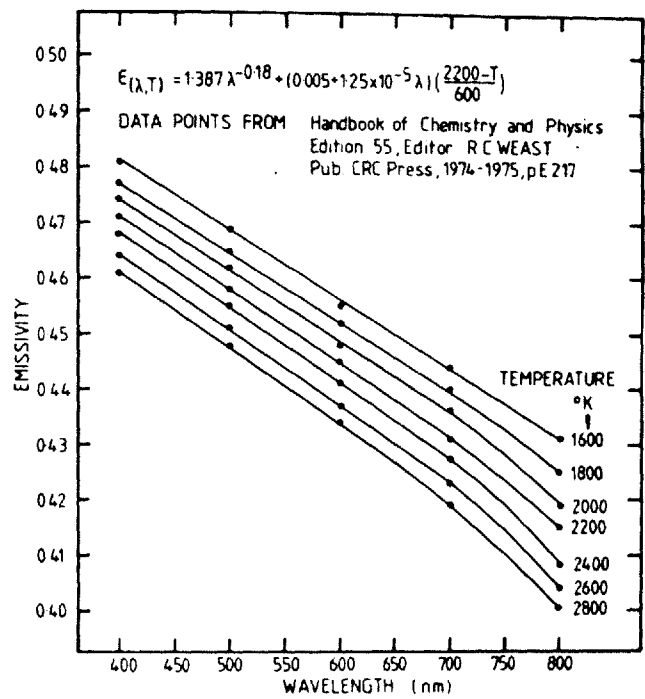


Figure 3.8: Spectral emissivity of tungsten at temperatures from 1600 to 2800°K.

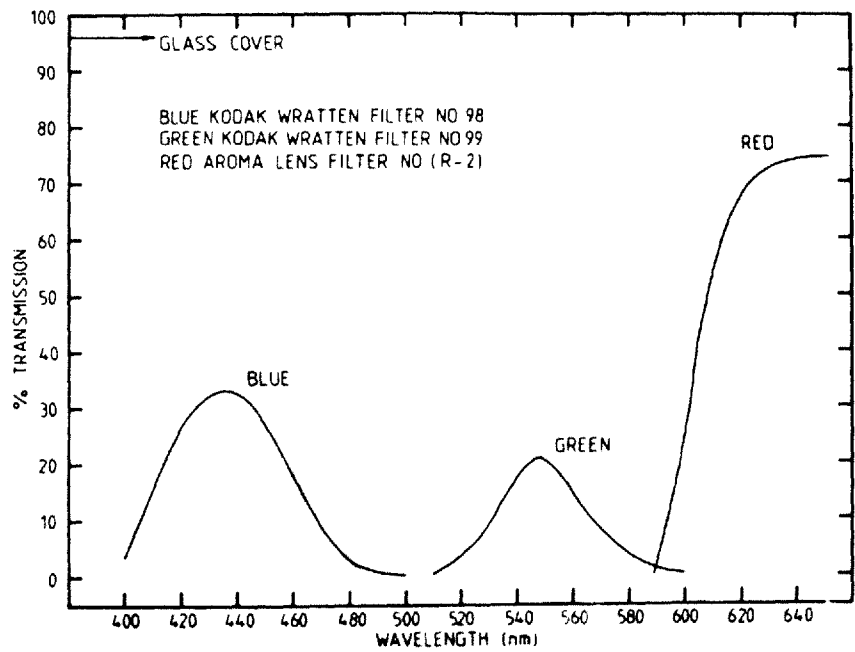


Figure 3.9: Spectral transmission of Blue, Green and Red filters and a glass cover side.

- (4) The film exposure depends on the effective aperture diameter and the shutter speed. The radiation transmitted to the film is reduced by an amount equal to:

$$\frac{\text{shutter speed}}{(\text{effective } f)^2} \quad \dots (3.12)$$

and this parameter is termed the 'exposure factor'.

- (5) The spectral response (termed "sensitivity") of the film is dependent on the wavelength of the incident radiation (Figure 3.10).
- (6) The density upon development changes with the developing schedule (Figure 3.11).

The film density after exposure and development was determined in the following manner.

- (1) The spectral irradiance ( $\text{Watt m}^{-2} \text{ nm}^{-1}$ ) emitted from the tungsten filament was calculated by using Planck's law.

$$N_{\lambda} = \frac{3.7403 \times 10^{-16}}{\lambda^5 \exp\left(\frac{1.43879 \times 10^{-2}}{\lambda T} - 1\right)} e(\lambda, T) \quad \dots (3.3)$$

- (2) The spectral irradiance at 10 nm wavelength increments was calculated after transmission through the filters, and the wavelength of maximum transmittance ( $\lambda_{\text{max}}$ ) noted (Figure 3.12 - full lines).
- (3) The film sensitivity at  $\lambda_{\text{max}}$  (from Figure 3.12(a)) was used as a basis to calculate a 'sensitivity factor' (Table 3.3). Thus, when exposing the film through a blue filter, an exposure of  $x/2.04$  seconds with radiation of 400 nm wavelength will have the same intensity as an exposure of  $x$  seconds for radiation of 450 nm. Therefore the spectral irradiance can again be adjusted to account for the film sensitivity (Figure 3.12 - broken lines).

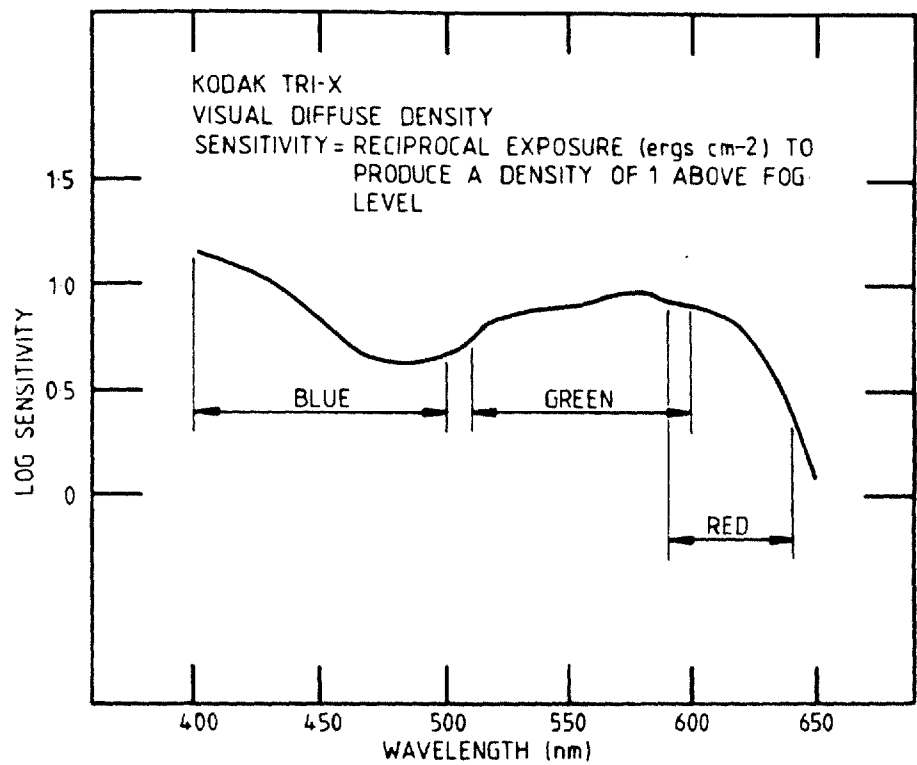


Figure 3.10: Spectral sensitivity of film.

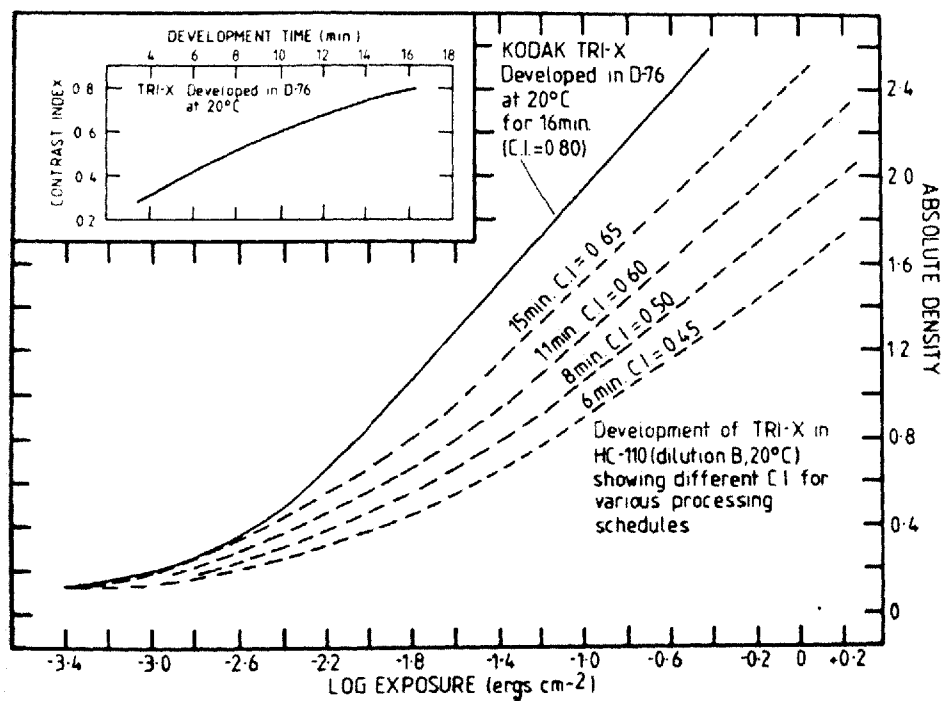


Figure 3.11: Absolute density - log exposure curve (D-log E) for Kodak Tri-X film.

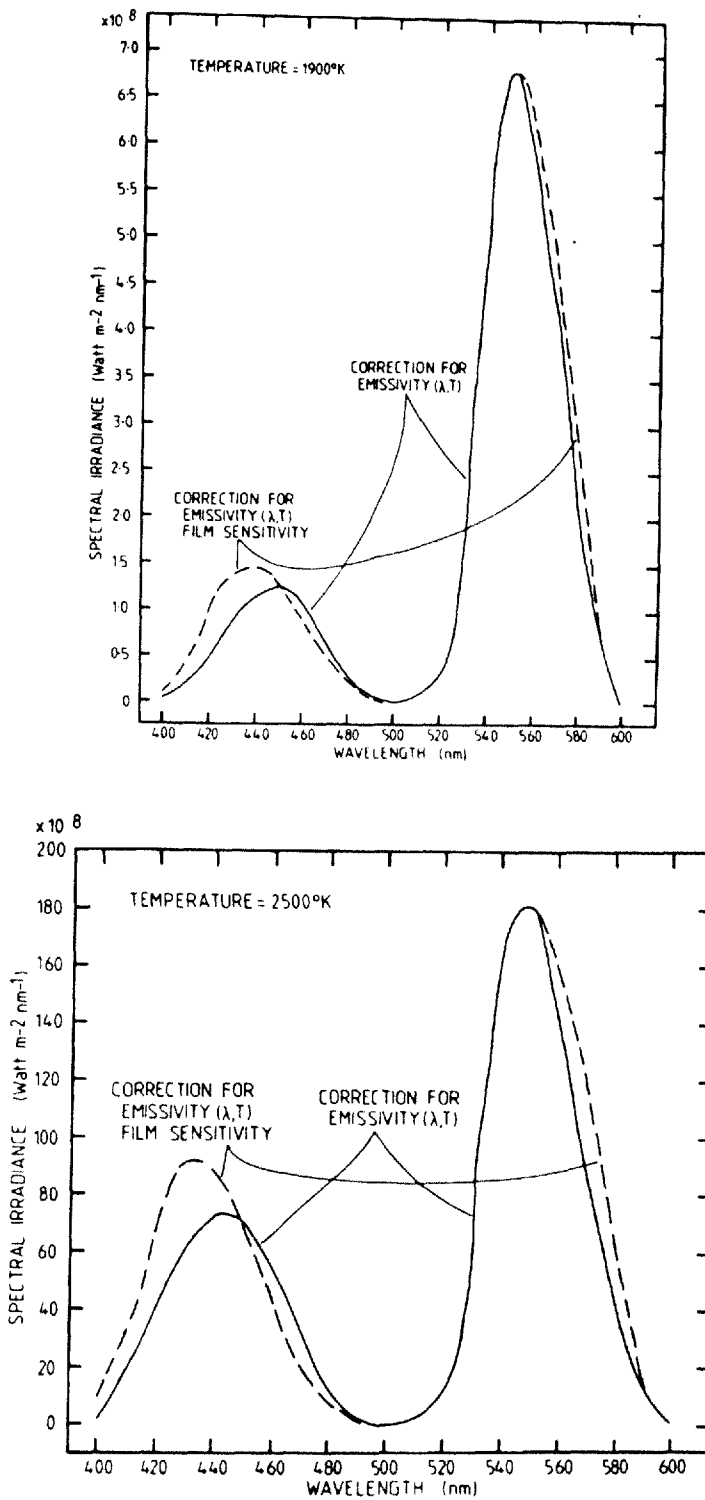


Figure 3.12: Effective spectral irradiance exposing film. Corrected for emissivity of source (full lines) and emissivity of source and film sensitivity (broken lines).

(a) at 1900 K

(b) at 2500 K.

**Table 3.3:** Combined sensitivity factors for blue, green and red radiation\* (taking into account the film response and filter transmission).

**Blue - relative to radiation of 450 nm.**

| $\lambda$<br>nm                                | Sensitivity | $\frac{1}{\text{exp}}$ sec <sup>-1</sup> | relative to<br>$\lambda = 450$ nm | %<br>transmission | Combined<br>Factor |
|------------------------------------------------|-------------|------------------------------------------|-----------------------------------|-------------------|--------------------|
| 400                                            | 1.15        | 14.13                                    | 2.04                              | 3.6               | 7.3                |
| 410                                            | 1.12        | 13.18                                    | 1.90                              | 13.5              | 25.7               |
| 420                                            | 1.08        | 12.02                                    | 1.74                              | 26.3              | 45.8               |
| 430                                            | 1.03        | 10.72                                    | 1.55                              | 32.4              | 50.2               |
| 440                                            | 0.94        | 8.71                                     | 1.26                              | 32.4              | 40.8               |
| 450                                            | 0.84        | 6.92                                     | 1.00                              | 26.9              | 26.9               |
| 460                                            | 0.74        | 5.50                                     | 0.79                              | 17.8              | 14.1               |
| 470                                            | 0.65        | 4.47                                     | 0.65                              | 8.7               | 5.7                |
| 480                                            | 0.62        | 4.17                                     | 0.60                              | 2.6               | 1.6                |
| 490                                            | 0.63        | 4.27                                     | 0.62                              | 0.5               | 0.3                |
| 500                                            | 0.65        | 4.47                                     | 0.65                              | 0                 | 0                  |
| <hr/>                                          |             |                                          |                                   |                   |                    |
| <b>Green - relative to radiation of 550 nm</b> |             |                                          |                                   |                   |                    |
| $\lambda = 550$ nm                             |             |                                          |                                   |                   |                    |
| 510                                            | 0.76        | 5.75                                     | 0.74                              | 0.5               | 0.4                |
| 520                                            | 0.84        | 6.92                                     | 0.89                              | 1.7               | 1.5                |
| 530                                            | 0.87        | 7.41                                     | 0.95                              | 8.5               | 8.1                |
| 540                                            | 0.88        | 7.59                                     | 0.98                              | 18.5              | 18.1               |
| 550                                            | 0.89        | 7.76                                     | 1.00                              | 19.5              | 19.5               |
| 560                                            | 0.94        | 8.71                                     | 1.12                              | 13.5              | 15.2               |
| 570                                            | 0.97        | 9.33                                     | 1.20                              | 8.0               | 9.6                |
| 580                                            | 0.97        | 9.33                                     | 1.20                              | 3.5               | 4.2                |
| 590                                            | 0.92        | 8.32                                     | 1.07                              | 1.0               | 1.1                |
| 600                                            | 0.90        | 7.94                                     | 1.02                              | 0                 | 0                  |
| <hr/>                                          |             |                                          |                                   |                   |                    |
| <b>Red - relative to radiation of 630 nm</b>   |             |                                          |                                   |                   |                    |
| $\lambda = 630$ nm                             |             |                                          |                                   |                   |                    |
| 590                                            | 0.92        | 8.32                                     | 1.91                              | 1.1               | 2.1                |
| 600                                            | 0.90        | 7.94                                     | 1.82                              | 22.9              | 41.6               |
| 610                                            | 0.86        | 7.24                                     | 1.66                              | 53.7              | 89.1               |
| 620                                            | 0.80        | 6.31                                     | 1.45                              | 67.6              | 98.0               |
| 630                                            | 0.64        | 4.37                                     | 1.00                              | 72.4              | 72.4               |
| 640                                            | 0.38        | 2.40                                     | 0.55                              | 72.4              | 39.8               |
| 650                                            | 0.05        | 1.12                                     | 0.26                              | 72.4              | 18.6               |

\* Note Blue and Green filters were used in the film calibration (section 3.3.1).

Blue and Red filters were used for measurements on particles in a plasma (section 3.3.2).

- (4) The total irradiance received by the film ( $\text{Watt m}^{-2}$ ) can be established from the area under the spectral irradiance vs wavelength curve (Table 3.4).
- (5) The energy density ( $\text{J m}^{-2}$ ) received by the film was found by multiplying by the exposure factor (Table 3.5). Before this energy density value can be used to find the film density the D-Log E curve for the relevant processing schedule must be determined, and the "log exposure" axis of this curve calibrated with respect to the incident radiation. Thus -
- (6) The D-log E curve can be extrapolated from the standard data (Figure 3.11) where the contrast index is 0.80 (Arnold et al., 1971, p.49).
- (7) The log exposure axis is calibrated by taking into account the film sensitivity data. The sensitivity at  $\lambda_{\text{max}}$  allows the exposure for a density of 1 above fog to be found and this value can also be determined from the D-log E curve. Thus the log E axis has been calibrated in terms of absolute units for radiation of  $\lambda_{\text{max}}$ .
- (8) The energy density which was calculated in step 5 can now be used to establish the 'theoretical' density after development (Table 3.6). Figure 3.13 shows how the theoretical density varies with the measured density and Figure 3.14 compares the response ratios.

Table 3.4: Total Irradiance received by Film  
(Watt m<sup>-2</sup>)

| T (K) | Blue  | Green | Red    |
|-------|-------|-------|--------|
| 1900  | 6.9   | 28.5  | 317.3  |
| 2000  | 16.2  | 56.1  | 580.7  |
| 2100  | 35.1  | 103.7 | 1002.8 |
| 2200  | 71.1  | 181.2 | 1647.4 |
| 2300  | 135.6 | 301.4 | 2590.9 |
| 2400  | 244.9 | 480.6 | 3922.7 |
| 2500  | 422.1 | 738.0 | 5743.2 |

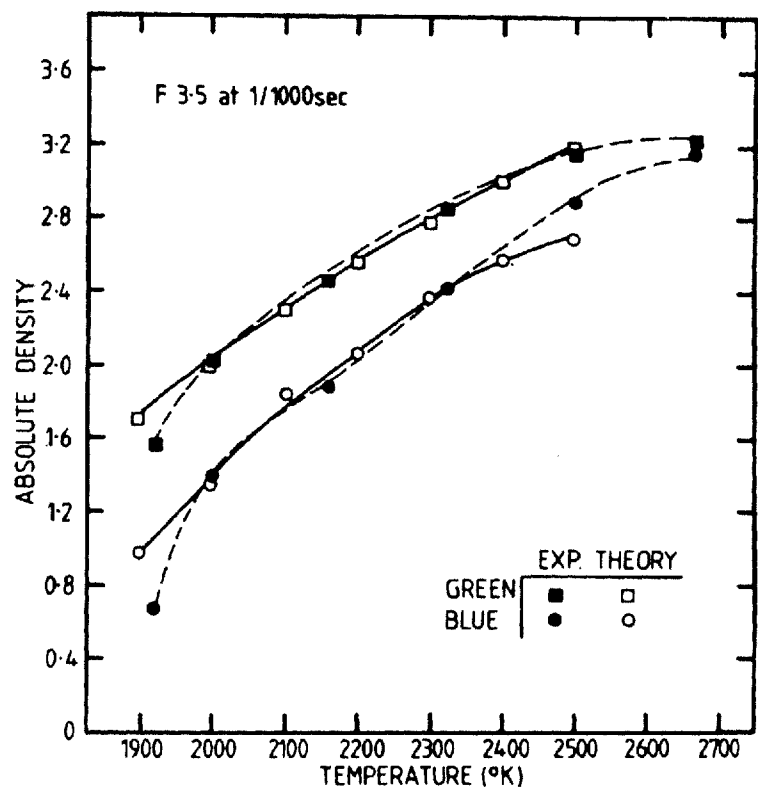
Table 3.5: Exposure Factors

| f-number | f(effective)* | Shutter Speed | Exposure Factor        |
|----------|---------------|---------------|------------------------|
| 3.5      | 8.3           | 1/1000        | $14.56 \times 10^{-6}$ |
| 5.6      | 13.3          | 1/500         | $11.38 \times 10^{-6}$ |
| 5.6      | 13.3          | 1/1000        | $5.69 \times 10^{-6}$  |
| 8        | 18.9          | 1/1000        | $2.79 \times 10^{-6}$  |

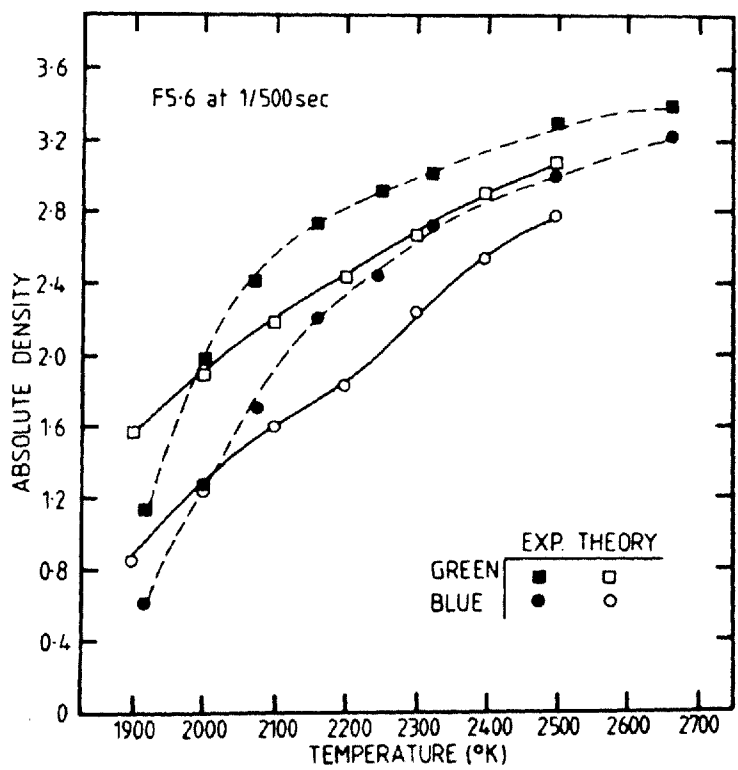
\* The magnification factor from the tungsten filament to the film was 1.37 and this is used in equation (3.11) to find f(effective).

Table 3.6: Theory Calculations of Film Exposure and Density

| <u>F3.5 at 1/1000 sec.</u> |              |         |              |         |          |
|----------------------------|--------------|---------|--------------|---------|----------|
| Temp. (K)                  | Blue         |         | Green        |         | Response |
|                            | log exposure | Density | log exposure | Density | Ratio    |
| 1900                       | -1.00        | 0.98    | -0.38        | 1.70    | 0.58     |
| 2000                       | -0.63        | 1.34    | -0.09        | 2.00    | 0.67     |
| 2100                       | -0.29        | 1.84    | 0.18         | 2.30    | 0.80     |
| 2200                       | 0.02         | 2.06    | 0.42         | 2.56    | 0.80     |
| 2300                       | 0.30         | 2.37    | 0.64         | 2.78    | 0.85     |
| 2400                       | 0.55         | 2.57    | 0.84         | 3.00    | 0.86     |
| 2500                       | 0.79         | 2.68    | 1.03         | 3.15    | 0.85     |
| <u>F5.6 at 1/500 sec.</u>  |              |         |              |         |          |
| 1900                       | -1.11        | 0.84    | -0.49        | 1.57    | 0.54     |
| 2000                       | -0.74        | 1.23    | -0.19        | 1.89    | 0.65     |
| 2100                       | -0.40        | 1.60    | 0.07         | 2.19    | 0.73     |
| 2200                       | -0.09        | 1.83    | 0.31         | 2.43    | 0.75     |
| 2300                       | 0.19         | 2.24    | 0.54         | 2.68    | 0.84     |
| 2400                       | 0.45         | 2.54    | 0.74         | 2.90    | 0.88     |
| 2500                       | 0.68         | 2.78    | 0.92         | 3.08    | 0.90     |
| <u>F5.6 at 1/1000 sec.</u> |              |         |              |         |          |
| 1900                       | -1.41        | 0.56    | -0.79        | 1.25    | 0.45     |
| 2000                       | -1.04        | 0.90    | -0.50        | 1.55    | 0.58     |
| 2100                       | -0.70        | 1.27    | -0.23        | 1.85    | 0.69     |
| 2200                       | -0.39        | 1.74    | 0.01         | 2.12    | 0.82     |
| 2300                       | -0.11        | 1.91    | 0.23         | 2.36    | 0.81     |
| 2400                       | 0.14         | 2.20    | 0.44         | 2.58    | 0.85     |
| 2500                       | 0.38         | 2.45    | 0.62         | 2.75    | 0.89     |
| <u>F8 at 1/1000 sec.</u>   |              |         |              |         |          |
| 1900                       | -1.72        | 0.36    | -0.10        | 0.90    | 0.40     |
| 2000                       | -1.35        | 0.62    | -0.81        | 1.22    | 0.51     |
| 2100                       | -1.01        | 0.95    | -0.54        | 1.51    | 0.63     |
| 2200                       | -0.70        | 1.27    | -0.30        | 1.77    | 0.72     |
| 2300                       | -0.42        | 1.57    | -0.08        | 2.01    | 0.78     |
| 2400                       | -0.17        | 1.75    | 0.13         | 2.25    | 0.78     |
| 2500                       | 0.07         | 2.12    | 0.31         | 2.42    | 0.88     |



(a)



(b)

Figure 3.13(a and b): Experimental and theoretical measurements of film density after exposure through blue and green filters.  
(a) Camera conditions of F3.5 at 1/1000 sec.  
(b) Camera conditions of F5.6 at 1/500 sec.

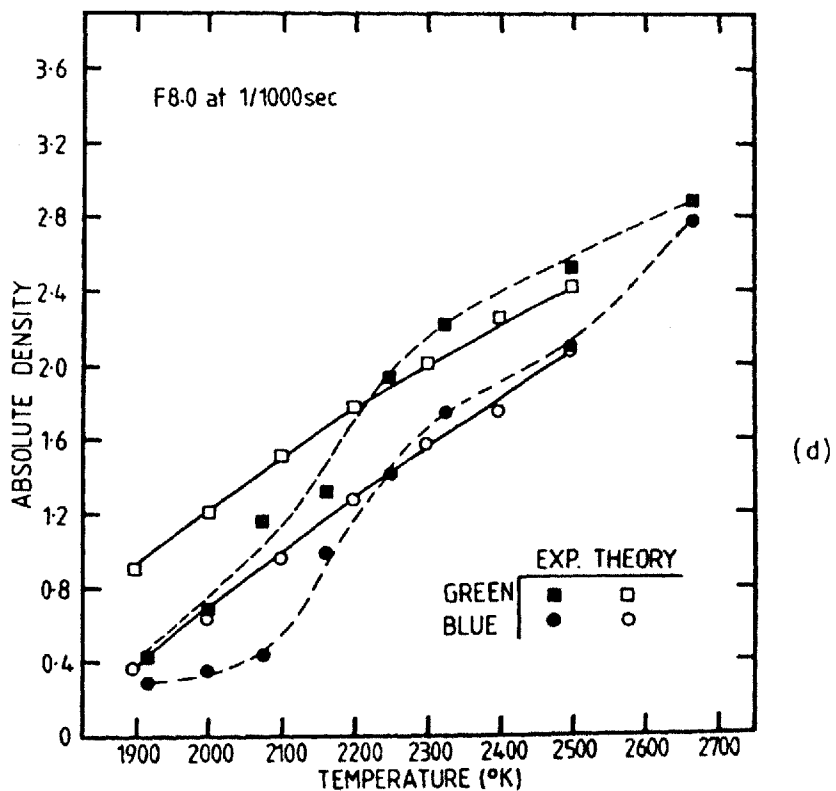
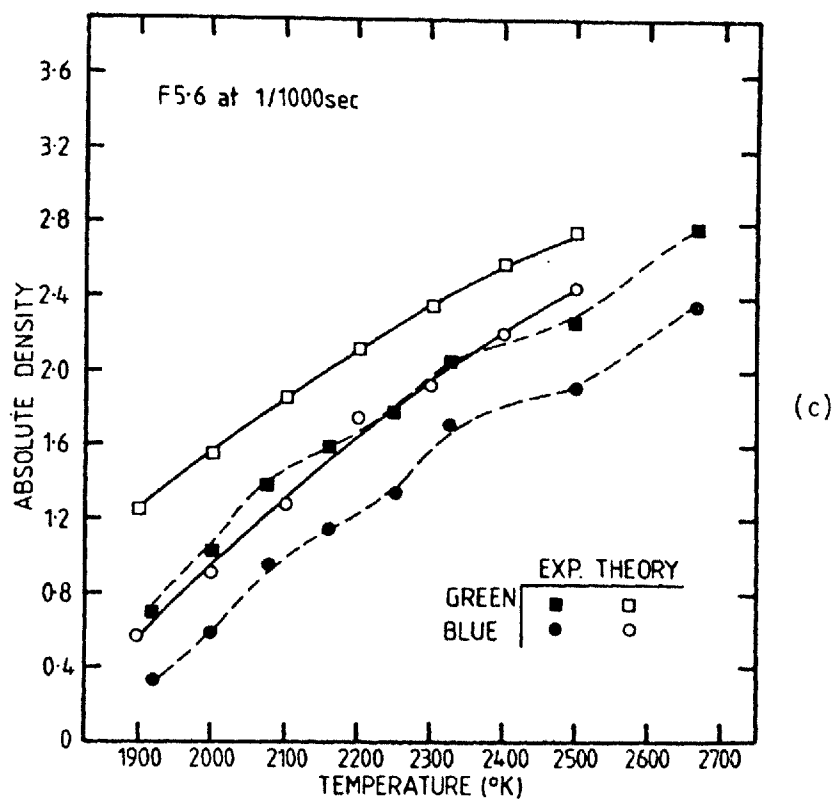


Figure 3.13(c and d): Experimental and theoretical measurements of film density after exposure through blue and green filters.

(c) Camera conditions of F5.6 at 1/1000 sec.

(d) Camera conditions of F8.0 at 1/1000 sec.

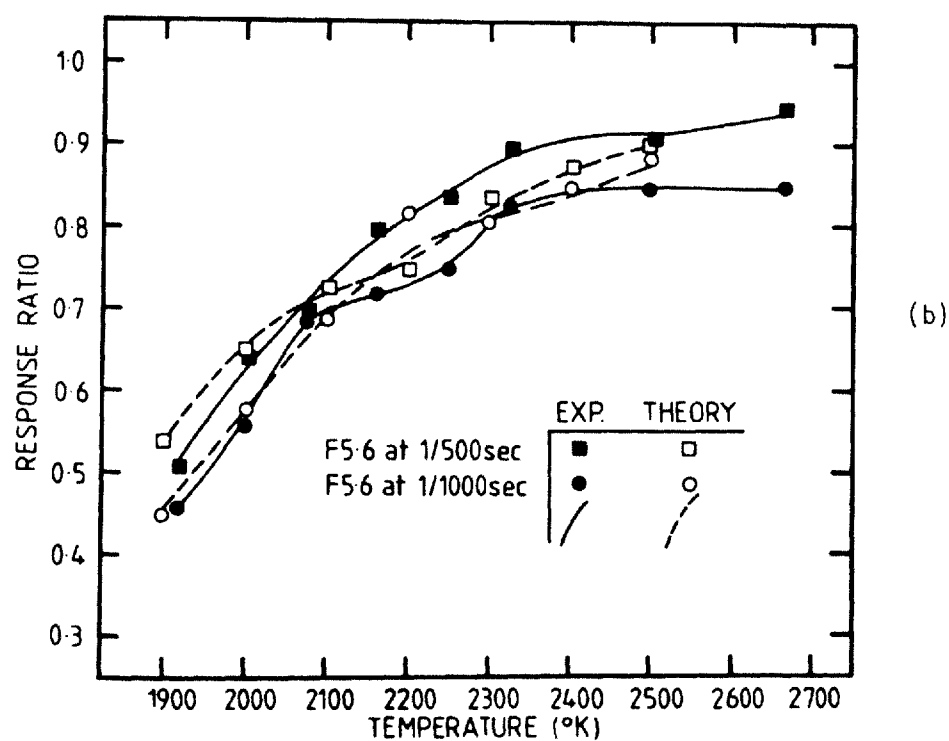
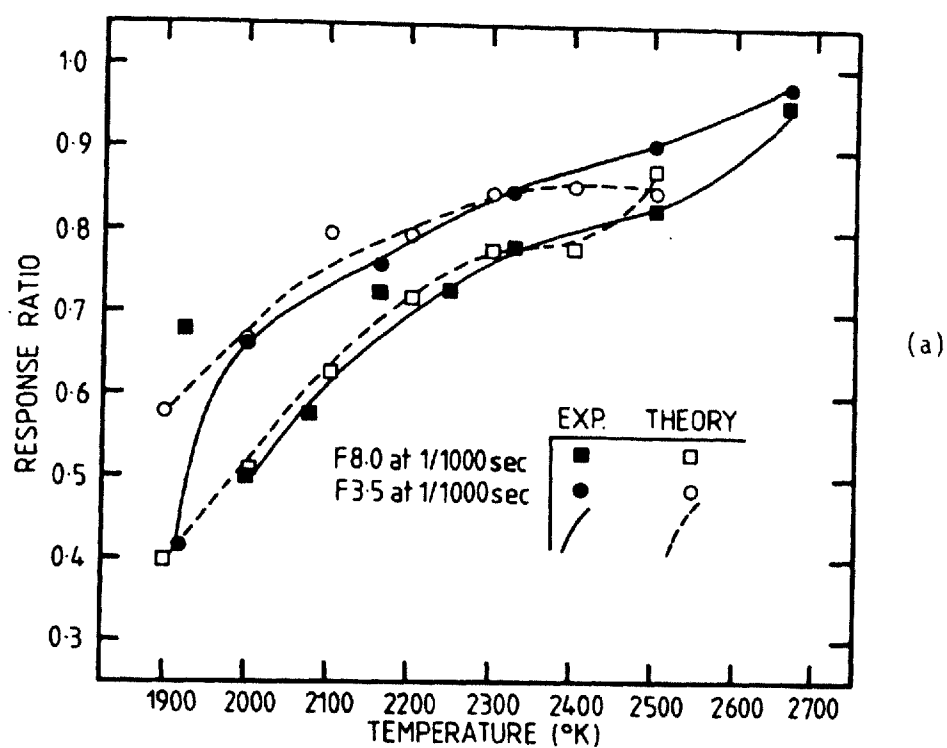


Figure 3.14(a and b): Experimental and theoretical measurements of the response ratio change (blue/green) with temperature.

- (a) Camera conditions of F8.0 at 1/1000 sec,  
F3.5 at 1/1000 sec.  
(b) Camera conditions of F5.6 at 1/500 sec,  
F5.6 at 1/1000 sec.

#### 3.3.1.4 Discussion

The density of film blackening by radiation emitted from a source is dependent on many factors which can be broadly classified under the following headings:

- (i) attenuation due to the filter and camera lens,
- (ii) exposure variations due to incorrect camera adjustment,
- (iii) chemical effects associated with the mechanism of film development and,
- (iv) the measurement of density.

The greatest error with the theoretical calculation of density would be associated with the estimation of the exposure time. Transmission losses of the incident radiation through the lens due to absorption in the lens material and reflection from the various air glass surfaces are negligible (Horder, 1963, p.75) with an average transmission of about 99%. However there would be expected to be about a 5% transmission loss of radiation emitted by the tungsten filament in passing through the glass envelope of the diode and a further loss of 5% is due to reflection from the filter. In most cases glass slides were used to protect the filter during the part of the work where molten particles were examined and this would attenuate the radiation by another 5%.

Other practical considerations concerning the optical system are that:

- (i) the f stop calibration may not be precise,
- (ii) the true exposure time of a focal plane shutter may vary according to the type of camera and its condition, and
- (iii) illumination effects over the lens field may vary (termed the 'vignetting effect') so that the image intensity, and thus film exposure, decreases towards the edge of the field of view. This effect is most serious when using small aperture openings, large focal length lens and bellows arrangements (Horder, 1963, p.79).

Several precautions (Arnold et al., 1971, pp.62-68) regarding the film should also be followed when it is intended to carry out a photothermographic experiment. The film for all of the experiments should preferably be from the same batch and this should be stored in a low humidity, low temperature environment and used near the end of its recommended shelf life so that any changes in its spectral characteristics are a minimum. It is important to maintain a standard development schedule and this should be carried out after the complete latent image has formed in the emulsion which is normally from 1 to 2 hours after exposure.

The film density after development may also change with slight variations in the emulsion thickness, local blemishes or chemical effects resulting from the exposure of small but high intensity sources. The latter effects can be classified as:

- (i) irradiation which results from scattering of the incident radiation,
- (ii) halation which occurs due to back reflection from the film base,
- (iii) adjacency effects (or "Eberhard" effects) which are caused by insufficient agitation during development and are manifested by a density change over an image area from point to point even though the exposure may be constant, and
- (iv) reciprocity failure of the film which occurs when the maximum film density is not achieved under high exposure conditions.

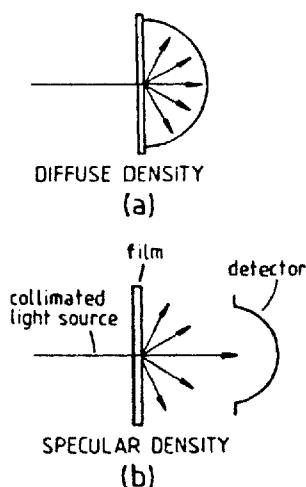
Another important factor is that the D-log E curve (Figure 3.11) is normally expressed in terms of "diffuse" density but the density measurement has a significant "specular" density component. The term diffuse density infers that all of the scattered and transmitted radiation is collected by the detector (Figure 3.15); whereas if only the normally emergent radiation is detected this is called the specular density. The specular density is always greater than the diffuse density and thus the ratio -

$$\frac{\text{specular density}}{\text{diffuse density}} = Q > 1 \quad \dots (3.13)$$

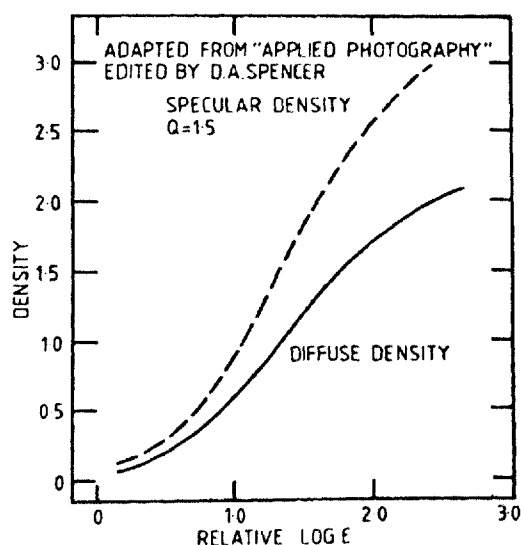
and this parameter is termed the Callier coefficient.

The diffuse density is not measured by the Joyce microdensitometer since the collecting angle is not  $\pm 90^\circ$  but dependent on the numerical aperture of the condenser lens and collecting objective. The Callier coefficient varies with film emulsion, development conditions and the wavelength of the incident radiation so that for high speed film it may reach values of about 1.7. The effect of high  $Q$  values is to displace the D-log E curve (Figure 3.16) and therefore the experimentally measured density (specular) will not agree with the theoretical calculation of the diffuse density.

Thus film is not a particularly sensitive medium for measuring temperature. The main problem is that the response varies with the exposure time (Figure 3.6) so it is necessary to use the absolute densities of the film response to determine the exposure time and temperature simultaneously. This technique is described in the following section.



**Figure 3.15:**  
Types of density measurement



**Figure 3.16:**  
Variation of density - log exposure curve for diffuse and specular density (Arnold et al., 1971, p.39).

### 3.3.2 Measurements on Particles Fed into a Plasma

#### 3.3.2.1 Introduction

The preceding section showed that the density ratio of film that had been exposed through two filters could be used to calculate the temperature of the source; but only if the exposure time of the source onto the film was known. This section describes the use of the photothermographic technique to calculate the temperatures and speeds of mild steel particles fed into a DC plasma tail flame.

A major feature of the results was that the response ratio of a particle varied in a sinusoidal manner with position from the torch. This section is therefore devoted predominantly to the interpretation of the results and a comparison with theoretical predictions of radiated intensity and response ratio as a function of particle temperature and relative exposure time (or relative velocity).

#### 3.3.2.2 Experimental

The arrangement used for photographic experiments with the tungsten filament could not be used for particle photography because of drawbacks associated with the SLR camera. The operation of the focal plane shutter can lead to unequal exposure times over the field of view as well as distortion of the photographic image of rapidly moving events (Langford, 1969, p.77). Also the SLR camera used in this work has the additional drawback of exposing a small frame (35 x 24 mm) which presents practical difficulties in alignment and orientation under the microdensitometer. When photographing rapidly moving particles there is no need for the high shutter speeds that are usual for SLR cameras because the particle image will move across the frame of the film in a short time compared to the shutter speed. Thus it is not possible to "stop" the particle motion using conventional cameras and the only advantage of using short exposures is to prevent the overlapping of particle streaks so that the subsequent analysis is less complicated.

With these factors in mind the experimental arrangement was altered to incorporate a Linhof model camera (film size 45 x 55 mm) which has a between-the-lens shutter so that exposure conditions over the entire film frame are constant. It should be noted that the shutter efficiency increases with smaller apertures so that the relative opening and closing time of the shutter is negligible.

A dual image of the same event was obtained by fitting a stereoscopic attachment onto the front lens of the camera and various shields were erected around the plasma torch to prevent superposition of the images (Figure 3.17).

The particles were photographed against a black background into which holes had been drilled so that a light grid could be formed onto the film. These points served as reference marks that enabled microdensity plots to be carried out and the magnification (about 0.3) calculated.

The filters were incorporated into lens caps which fitted over the stereo attachment and a blue/red combination used (instead of the blue/green filters used in section 3.3.1) since it has been

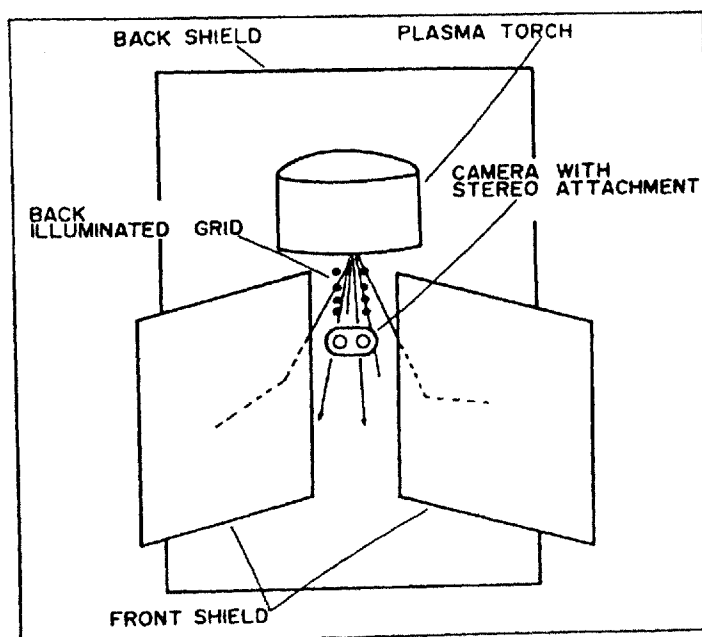


Figure 3.17: Schematic of experimental arrangement to record stereoscopic images of particle streaks.

reported (Hornbeck, 1966) that the sensitivity of the two colour method increases with separation in the wavelengths.

The torch, powder type and feed, and camera conditions were chosen to increase the exposure time of the particles - these corresponded to low arc gas flow rates, low carrier gas flow rates and large particle size, and exposure times of  $1/250$  sec at f5.6. Tri-X film (ex Kodak) developed in D76 at 20°C for 16 minutes was used.

### 3.3.2.3 Results

A suitably exposed film for microdensitometer analysis was obtained with an aperture opening of f5.6 and a print of this film is shown in Figure 3.18. The streaks through the blue filter (left half of the figure) are not as well defined as those through the red filter. Also it can be seen that the image through the red filter is slightly displaced (by about 1.5 cm at the source) with respect to the blue filter since the grid markers are not horizontally aligned. The left hand side of the markers for the red exposure is not present due to the position of the shields.

The film was enlarged and tracings of the individual streaks made in order to facilitate matching of the two images (Figure 3.19). The procedure shown in the inset of Figure 3.19 was followed when measuring the density of a streak as a function of distance, using the microdensitometer. The analysis area of the source can be calculated from the expression:

$$\begin{aligned} & \frac{\text{slit height}}{\text{magnification of objective}} \times \frac{1}{\text{magnification factor}} \\ & \text{in densitometer} \quad \text{of camera lens} \\ & = \frac{1.1}{4 \times 0.33} \quad \dots (3.14) \\ & = 0.825 \text{ mm} \end{aligned}$$

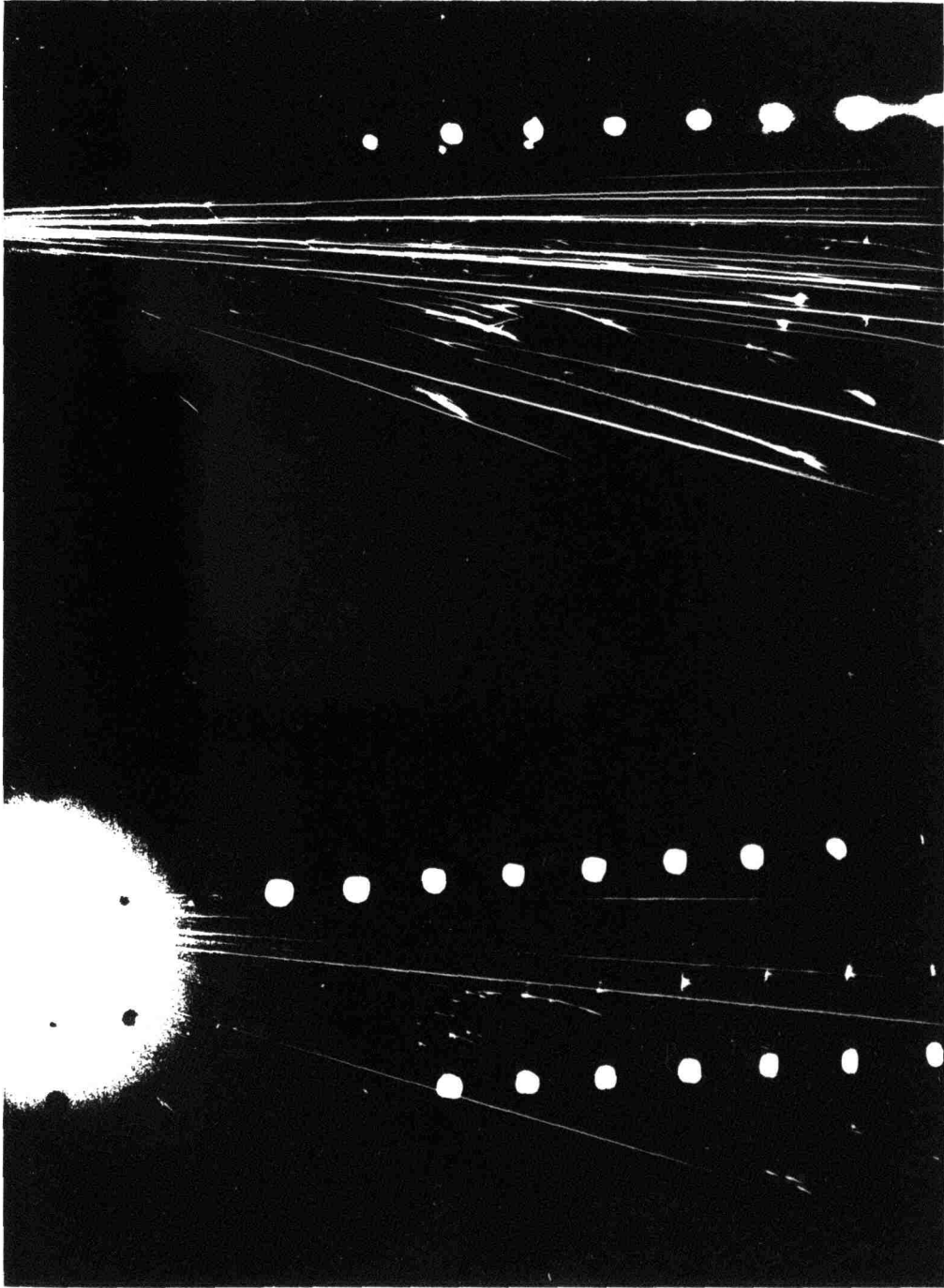


Figure 3.18: Stereoscopic image of particle streaks (left hand side exposed through blue filter and right hand side exposed through red filter).

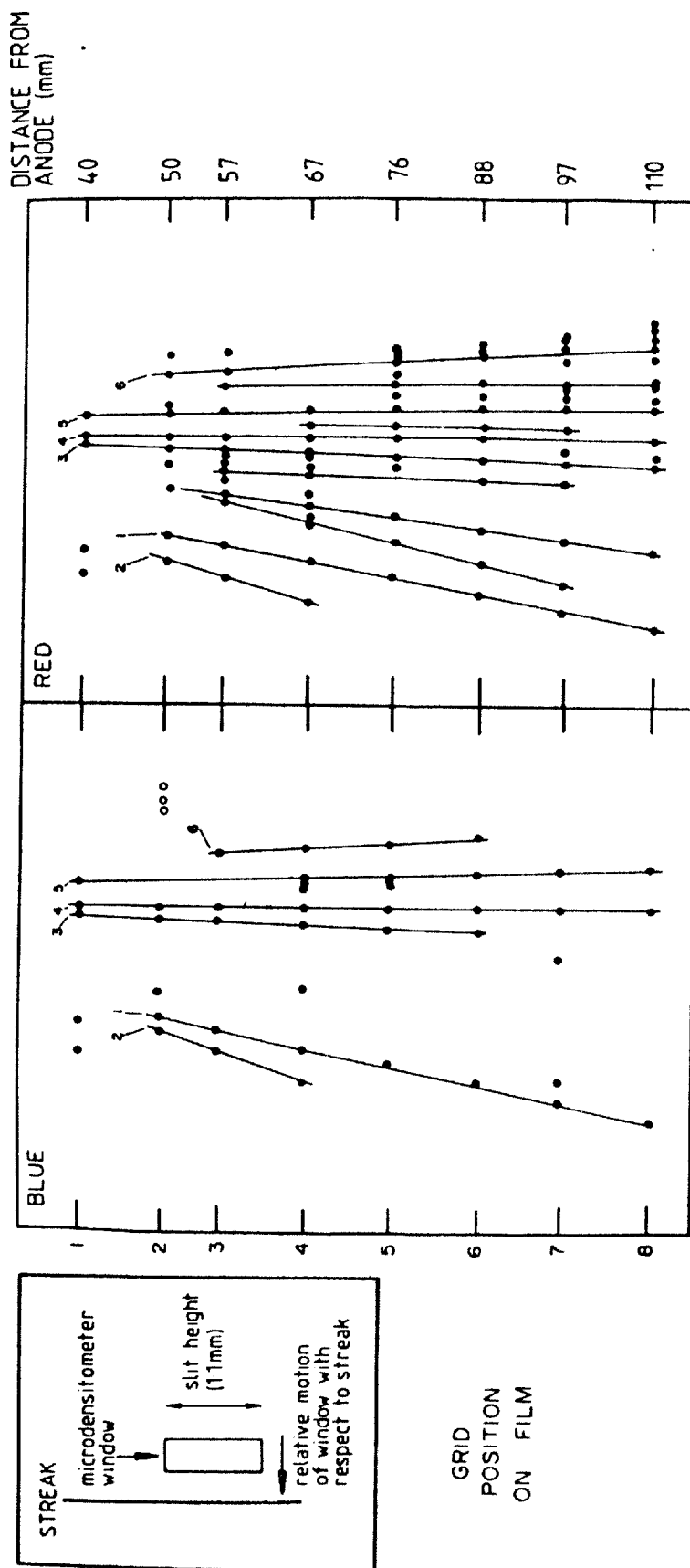


Figure 3.19: Microdensity recordings of particle streaks  
Inset shows the measuring procedure.

The absolute densities of 6 streaks (above fog level) are shown in Figure 3.20 (Table 3.7) and the variation of the blue/red density ratio in Figure 3.21. The predominantly sinusoidal nature of the curves for each particle is examined below.

### 3.3.2.4 Comparison with Theoretical Calculations

The expected film density can also be calculated as in the previous section, but several additional factors must be taken into account. No data on the spectral emissivity of iron within the visible wavelength range and at temperatures from 1900 to 2500°K is available and therefore two extreme cases were examined. The spectral emissivity of iron near to its melting point is about 0.35 whereas at high temperatures it will oxidise so that  $\epsilon = 0.70$ . The radiation will be attenuated by up to 20% on transmission through the filters and stereoscope due to absorption and reflection effects. Also the camera was used at an aperture of f5.6 and this reduces the radiation intensity by a factor of 1/32.

The particle velocity is significantly greater than the shutter speed so therefore the film exposure time is dependent on the writing speed of the particles onto the film. The microdensity values represent measurements over a length of 0.825 mm at the source so therefore the velocity (V) of the particle will be :

$$V = \frac{0.825 \times 10^{-3}}{t_{\text{exp}}} \text{ m sec}^{-1} \quad \dots (3.15)$$

where  $t_{\text{exp}}$  is the effective exposure time (in seconds). Large errors can result due to uncertainty in the emissivity and transmission factors so maximum and minimum values of exposure conditions were considered in order to establish the relative error in the response ratio calculation. The average emissivity of the mild steel particles varies from approximately 0.35 for the metal to 0.70 for the oxide and the transmission factor for the lens is assumed to be 80%. The expected blue/red response ratio for different exposure times and temperatures can be calculated (Appendix 3, Figure 3.22) where it can be seen to vary by up to about 0.1 due to uncertainties in the emissivity.

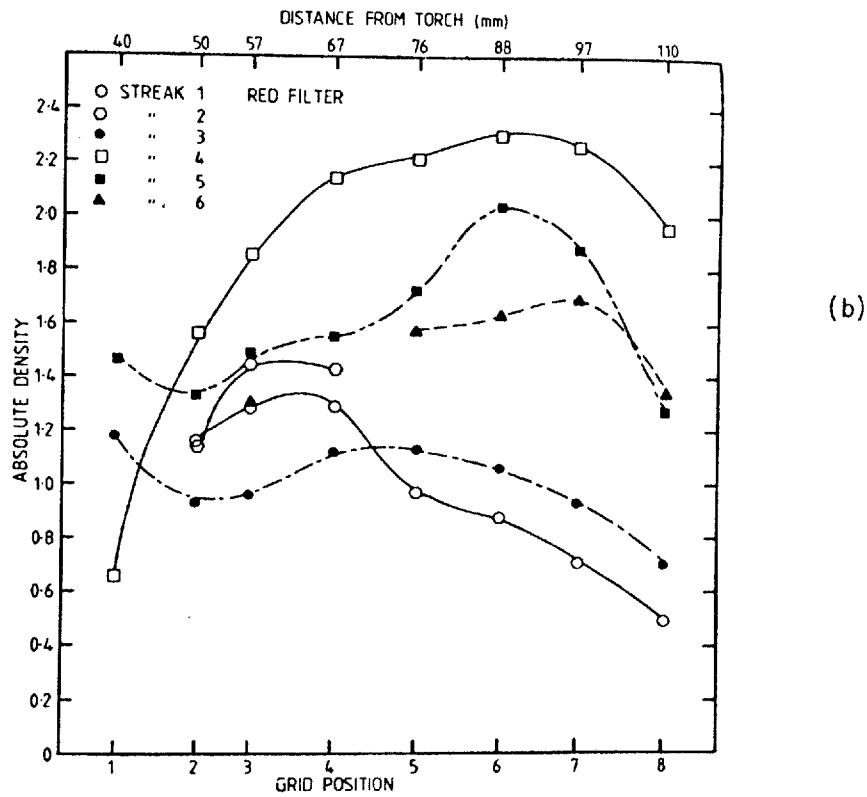
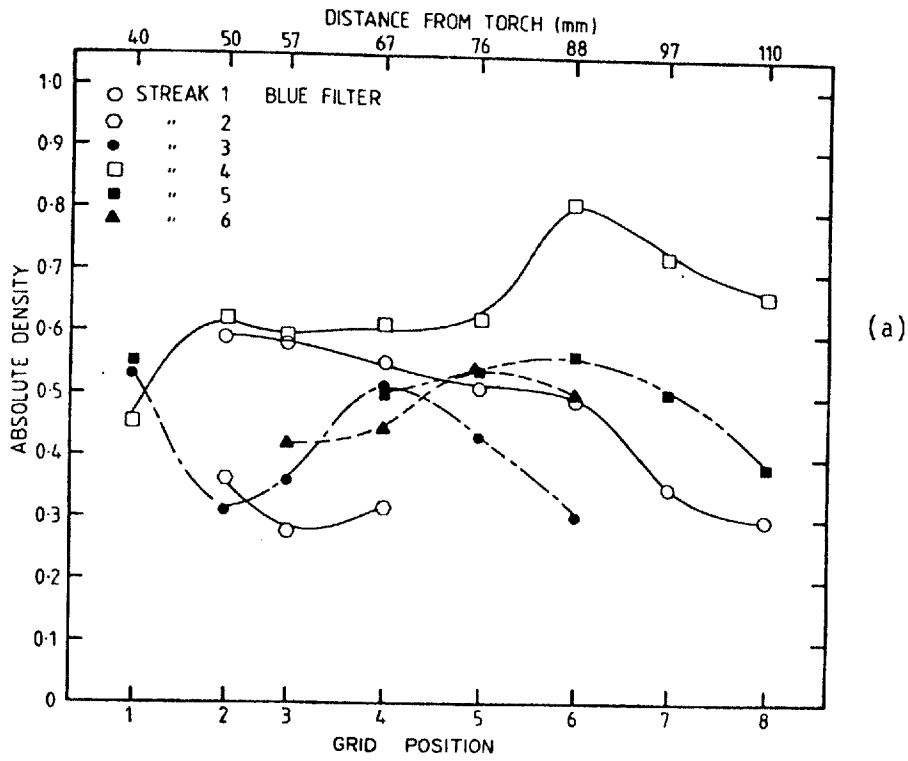


Figure 3.20: Absolute density measurements on particle streaks  
 (a) through blue filter.  
 (b) through red filter.

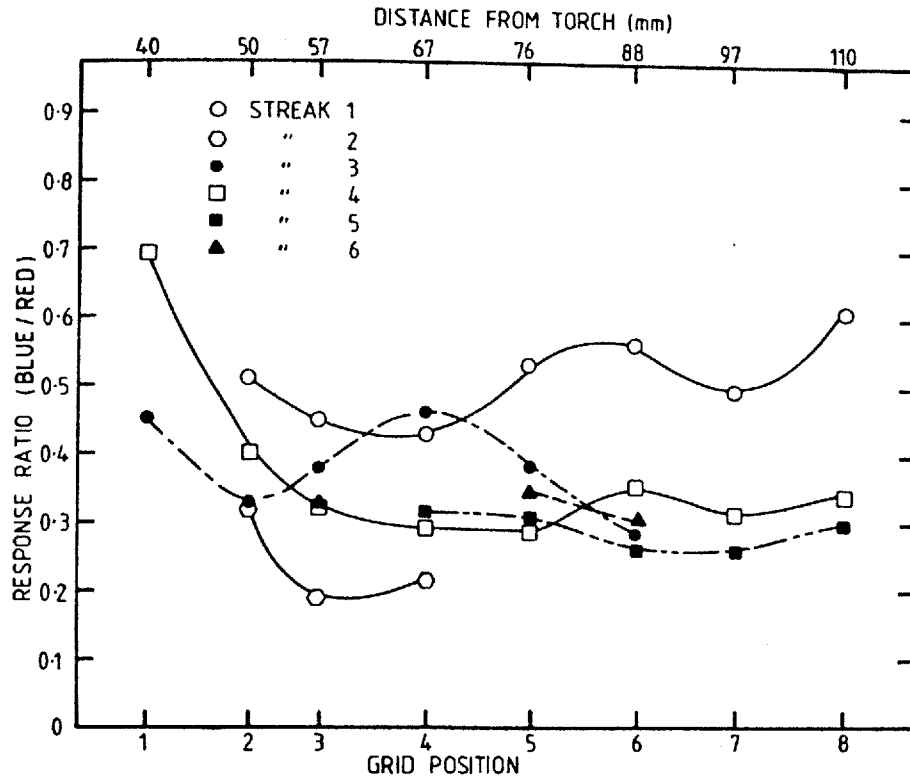


Figure 3.21: Response ratio (blue/red) of particle streaks

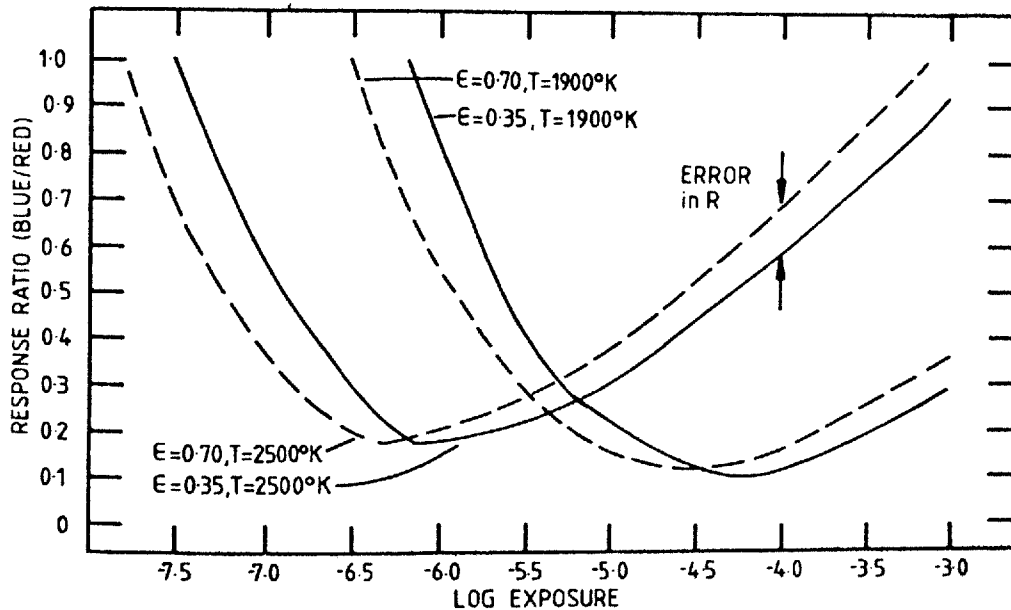


Figure 3.22: Calculated response ratio versus log exposure curves for particles of emissivity 0.35 (full lines) and 0.70 (broken lines) at temperatures of 1900°K and 2500°K.

Table 3.7: Absolute densities and response ratios of particles streaks

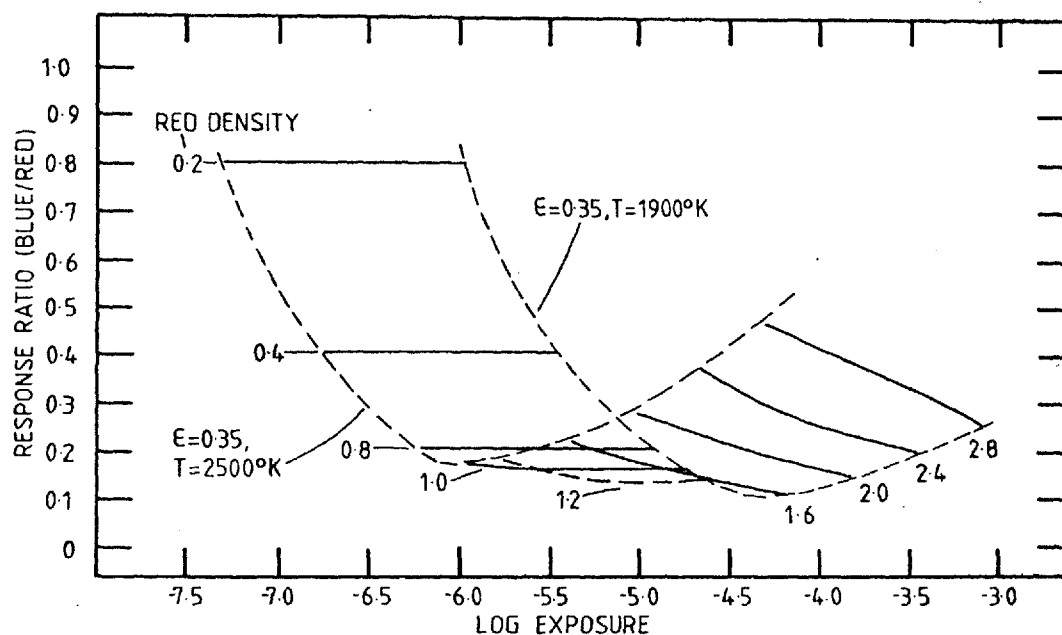
| Position | STREAK 1    |              |                | STREAK 2    |              |                | STREAK 3    |              |                |
|----------|-------------|--------------|----------------|-------------|--------------|----------------|-------------|--------------|----------------|
|          | Red Density | Blue Density | Response Ratio | Red Density | Blue Density | Response Ratio | Red Density | Blue Density | Response Ratio |
| 1        | -           | -            | -              | -           | -            | -              | 1.18        | 0.53         | 0.45           |
| 2        | 1.16        | 0.59         | 0.51           | 1.14        | 0.36         | 0.32           | 0.93        | 0.31         | 0.33           |
| 3        | 1.28        | 0.58         | 0.45           | 1.45        | 0.28         | 0.19           | 0.96        | 0.36         | 0.38           |
| 4        | 1.29        | 0.55         | 0.43           | 1.43        | 0.32         | 0.22           | 1.12        | 0.51         | 0.46           |
| 5        | 0.97        | 0.51         | 0.53           | -           | -            | -              | 1.13        | 0.43         | 0.38           |
| 6        | 0.88        | 0.49         | 0.56           | -           | -            | -              | 1.06        | 0.30         | 0.28           |
| 7        | 0.71        | 0.35         | 0.49           | -           | -            | -              | 0.93        | -            | -              |
| 8        | 0.49        | 0.30         | 0.61           | -           | -            | -              | 0.70        | -            | -              |
|          |             |              |                |             |              |                |             |              |                |
|          | STREAK 4    |              |                | STREAK 5    |              |                | STREAK 6    |              |                |
|          | Red Density | Blue Density | Response Ratio | Red Density | Blue Density | Response Ratio | Red Density | Blue Density | Response Ratio |
| 1        | 0.65        | 0.45         | 0.69           | 1.46        | 0.55         | 0.38           | -           | -            | -              |
| 2        | 1.56        | 0.62         | 0.40           | 1.33        | -            | -              | -           | -            | -              |
| 3        | 1.85        | 0.59         | 0.32           | 1.49        | -            | -              | 1.30        | 0.42         | 0.32           |
| 4        | 2.14        | 0.61         | 0.29           | 1.55        | 0.50         | 0.32           | -           | 0.44         | -              |
| 5        | 2.21        | 0.62         | 0.28           | 1.72        | 0.53         | 0.31           | 1.57        | 0.53         | 0.34           |
| 6        | 2.30        | 0.81         | 0.35           | 2.04        | 0.56         | 0.27           | 1.63        | 0.49         | 0.30           |
| 7        | 2.26        | 0.72         | 0.32           | 1.87        | 0.50         | 0.27           | 1.69        | -            | -              |
| 8        | 1.95        | 0.66         | 0.34           | 1.27        | 0.38         | 0.30           | 1.34        | -            | -              |

The increasing response ratio at short exposure times arises due to the attainment of only the minimum development (which is the fog level of 0.16) for the film exposed through the blue filter. The response ratio is the same at the intersection point of two curves representing two different temperatures, but the absolute densities will be greater for the higher temperature. Thus it is possible (Figure 3.23) to show the relationship of exposure and response ratio for a specific film density through one of the filters. It can be seen that for red densities less than 1 the response ratio does not change over a wide range of exposure conditions because the film is not exposed through the blue filter to density values above the fog level.

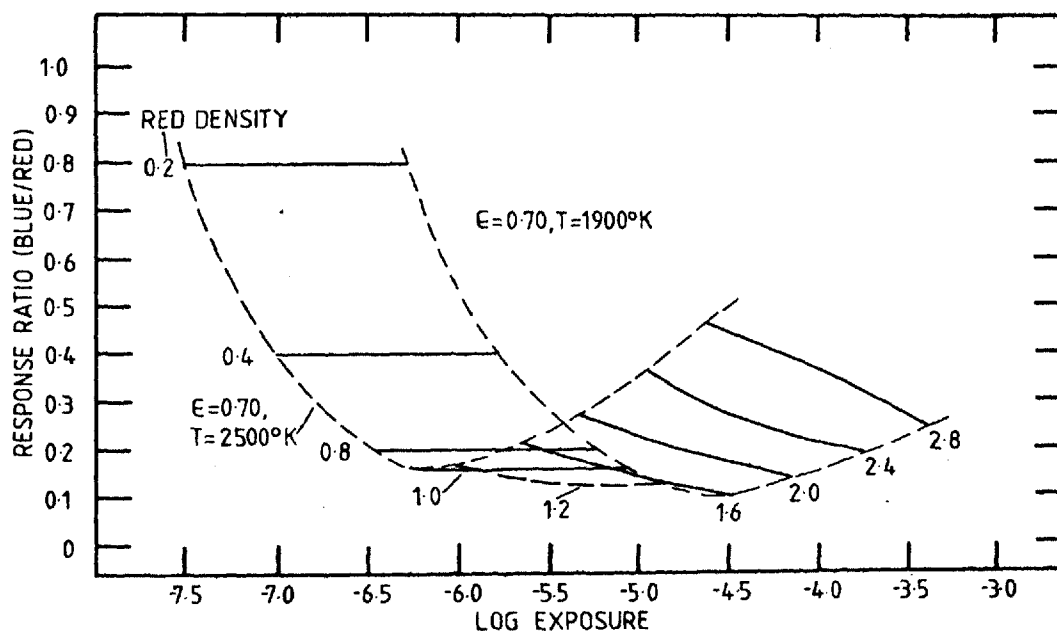
The exposure axis can also be expressed in terms of particle velocity by applying the relation 3.15 and velocities of 10 to 100 m sec<sup>-1</sup> are implied at exposure times of about 10<sup>-4</sup> to 10<sup>-5</sup> seconds. However it should be kept in mind that the exposure calculations are dependent on assumptions which include:

- (i) the radiation from the particles is only attenuated by 20% on passing through the filters and lens and that this is equal for both the red and blue systems;
- (ii) the radiation is not attenuated by the plasma gases which envelope the particles, and
- (iii) the particle emissivity does not change with the wavelength of radiation or the particle temperature.

The velocities then should only be used as an indication of the range of particle speeds. The absolute red density was in some cases less than 1 so that it is possible for the exposure time to lie on the left hand side of the minimum response ratio.



(a) particle emissivity = 0.35.



(b) particle emissivity = 0.70.

Figure 3.23 (a and b): Full lines show the calculated response ratio versus log exposure curves when particles expose film to a specified density. Broken lines show the temperature and emissivity effects on the response ratio for specific exposures (as in Fig. 3.22).

The sinusoidal nature of Figure 3.21 is a true effect since the absolute densities of film exposed through both the red and blue filters vary in a similar fashion as smooth functions of distance from the torch. The increasing and then decreasing change in density can result because density is dependent on both temperature and particle speed. Thus a high temperature particle which initially has a high velocity may result in the same low density as a slow but much cooler particle. Maximum exposure conditions therefore occur at some intermediate temperature and velocity and there is a gradual transition about this maximum.

The sinusoidal shape of the curves can therefore be explained in a number of ways.

- (1) The shape arises due to irregularities in the film exposure which may come about from distortion of the lens field to produce the vignetting effect. Thus regions towards the lens edge may be underexposed with respect to the centre field of view and this effect will be altered further by the stereoscopic attachment. Film exposure by radiation from the plasma gas has not been taken into account and this would decrease away from the torch.
- (2) The response ratio may increase, decrease or remain constant with respect to the exposure conditions in the manner shown in Figure 3.24a. The various paths (1-9) taken by the particle represent the thermal and velocity histories so that both the temperature and velocity of the particle decreases. The distinctions between these paths are:
  - (i) Paths 1 to 3 are to the left of the response ratio and thus represent conditions where there is no film exposure above fog level through the blue filter.
  - (ii) Paths 4 to 6 are to the right of the response ratio minimum and represent conditions where there is film exposure through both the blue and red filters.
  - (iii) Paths 7 to 9 originate at the response ratio minimum and illustrate how there can be a transgression from paths

of type (i) to type (ii).

- (3) A similar effect in the response ratio is obtained if the emissivity of the particle changes (Figure 3.24b). The characteristics of these paths are summarised in Table 3.8.

Table 3.8: Density (red) and response ratio changes of particles

| Path Type                                                                  | Red Density<br>Change* | Response Ratio<br>Change* |
|----------------------------------------------------------------------------|------------------------|---------------------------|
| 1                                                                          | -                      | +                         |
| 2                                                                          | 0                      | 0                         |
| 3                                                                          | +                      | -                         |
| 4                                                                          | -                      | -                         |
| 5                                                                          | 0                      | -                         |
| 6i                                                                         | +                      | -                         |
| 6ii                                                                        | +                      | 0                         |
| 6iii                                                                       | +                      | +                         |
| 7                                                                          | -                      | +                         |
| 8                                                                          | +                      | +                         |
| 9                                                                          | +                      | -                         |
| 10                                                                         | +                      | -                         |
| 11                                                                         | +                      | +                         |
| *    - indicates decrease<br>+ indicates increase<br>0 indicates no change |                        |                           |

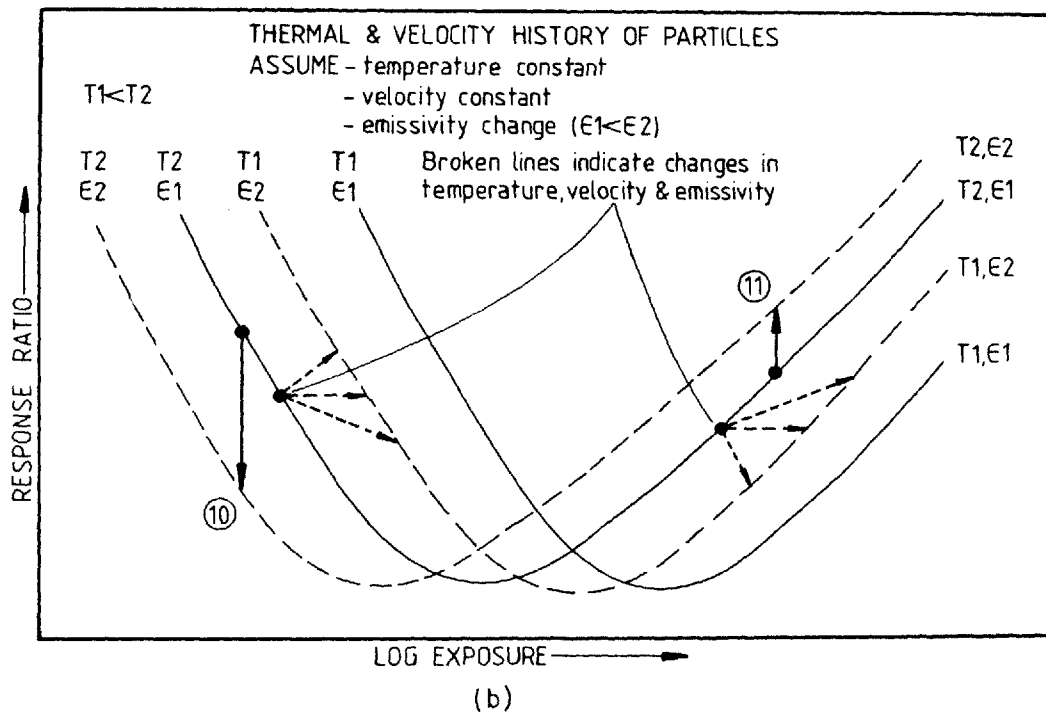
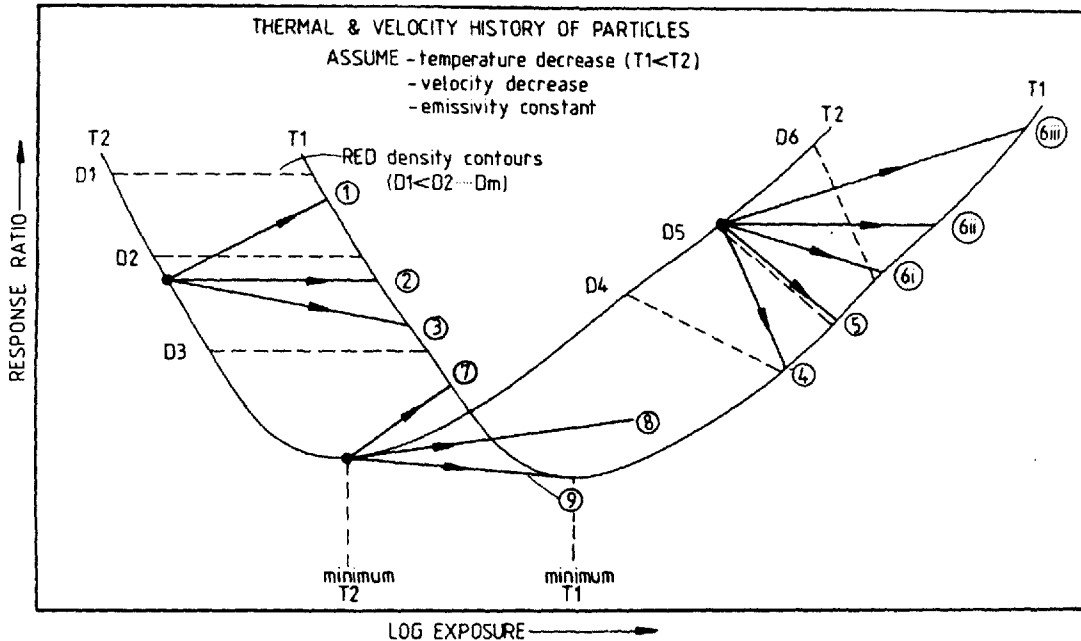


Figure 3.24: Schematic diagrams showing the response ratio change for particles with various thermal and velocity histories.

- (a) Temperature and velocity of particles decrease, emissivity is constant.
- (b) Full heavy lines - temperature and velocity is constant, emissivity changes. Broken lines - temperature and velocity of particles decrease and emissivity of particle increases.

Thus it is possible for the response ratio of a particle to vary with distance from the torch in a number of ways (Figure 3.25) by combination of the various paths. Variations of the response ratio resultant from emissivity changes are shown as occurring instantaneously at constant temperature but these are more likely to occur gradually as shown by the broken lines in Figure 3.24b.

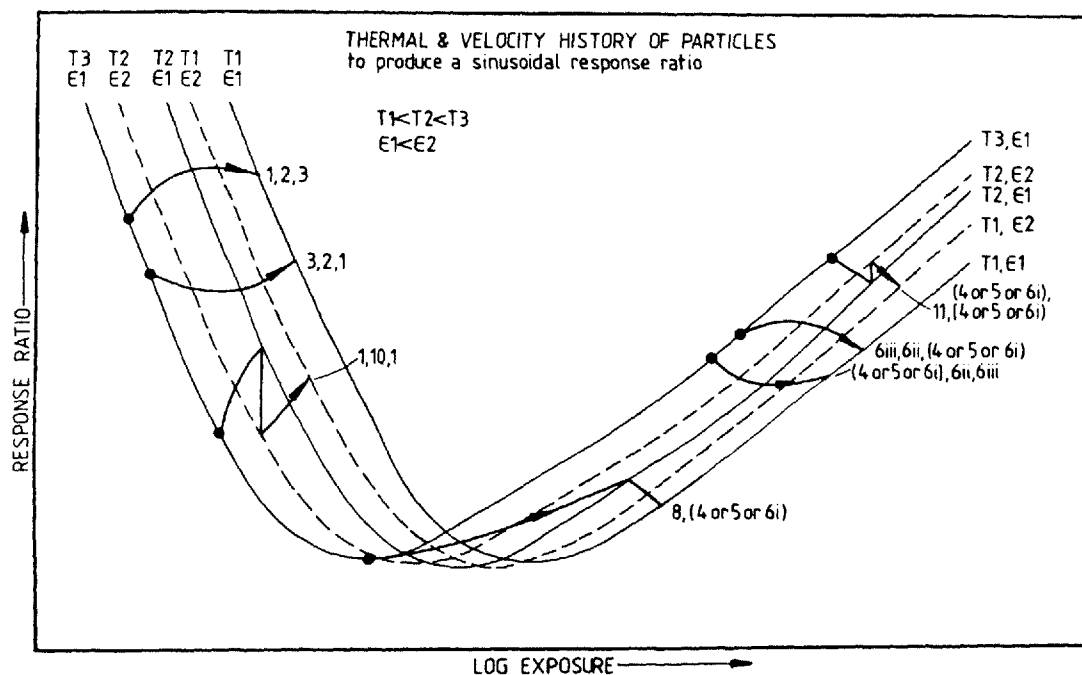


Figure 3.25: Thermal and velocity histories of particles to produce a sinusoidal response ratio.

### 3.3.2.5 Velocity and Temperature Calculations

The response ratio and absolute density of the particle can be used to measure the particle temperature and relative velocity. Therefore a set of exposures and temperatures can be calculated (as in Appendix 3) which will result in a specific red density and from these same conditions the blue density is also calculated. Thus the specific solution (exposure and temperature combination) is found from the intersection of this equi-density line with the response ratio that was initially measured. It can be seen that no single independent solution in the temperature range 1900 to 2500<sup>o</sup>K exists if the absolute red density is less than 1.0 (to the left of the minimum response ratio) since there is no film development through the blue filter. Therefore most of the readings taken from Table 3.7 are not within the useful range to allow their temperature and velocity (or exposure) measurement. The range can be extended by considering temperatures up to the boiling point of iron (3023<sup>o</sup>K) which also lowers the minimum red density requirement to 0.8. Streaks 2, 4, 5 and 6 were examined in this manner and the relative exposures and temperatures calculated as a function of distance from the torch (Table 3.9). The emissivity of the mild steel particles was assumed to be 0.35.

However it is most likely that the surface of particles would be oxidised at the temperatures of interest (2300 to 2900<sup>o</sup>K) where the trial gases mix with air. In this situation the particle emissivity is doubled and the prerequisite exposure condition to produce an intersection of the equi-density and response ratio lines is halved. Thus the overall effect of an emissivity increase is for the relative exposure determination to decrease. Choosing an emissivity of 0.35 gives a velocity distribution of 38 to 825 m sec<sup>-1</sup> (via expression 3.15) while an emissivity of 0.70 increases this estimation by a factor of two (76 to 1650 m sec<sup>-1</sup>).

It would be expected that the particles oxidise so the velocity range of 76 to 1650 m sec<sup>-1</sup> best represents the particle velocities for this work. Table 3.10 shows some values of the velocity determination selected from the literature and it can be seen that the upper field of the range (approximately 350 to 1650 m sec<sup>-1</sup>) found in

Table 3.9: Temperature, relative exposure and velocity of particles ( $\epsilon = 0.35$ )

| Grid<br>Position | Streak 2 |           |     | Streak 4 |      |     | Streak 5 |           |     | Streak 6 |           |     |
|------------------|----------|-----------|-----|----------|------|-----|----------|-----------|-----|----------|-----------|-----|
|                  | T        | t         | V   | T        | t    | V   | T        | t         | V   | T        | t         | V   |
| 1                | -        | -         | -   |          |      |     |          |           |     | -        | -         | -   |
| 2                |          | off scale |     |          |      |     |          |           |     | -        | -         | -   |
| 3                | 2425     | 3.3       | 250 | 2811     | 2.1  | 393 |          |           |     |          |           |     |
| 4                | 2593     | 1.7       | 485 | 2448     | 13.1 | 63  |          |           |     |          | off scale |     |
| 5                | -        | -         | -   | 2355     | 21.8 | 38  |          |           |     | -        | -         | -   |
| 6                | -        | -         | -   | 2490     | 15.6 | 53  | 2860     | 1.4       | 559 |          |           |     |
| 7                | -        | -         | -   | 2449     | 16.8 | 49  | 2427     | 11.5      | 72  | 2900     | 1.0       | 825 |
| 8                | -        | -         | -   | 2839     | 2.4  | 344 | 2540     | 5.2       | 159 | -        | -         | -   |
|                  |          |           |     |          |      |     |          | off scale |     | -        | -         | -   |

T = temperature (K)

t = relative exposure ( $\times 10^{-6} \text{ sec}^{-1}$ )

V = relative velocity ( $\text{m sec}^{-1}$ )

Table 3.10: Velocity measurements selected from the literature

| Reference                                | Powder Type                                                                              | Velocity in m sec <sup>-1</sup>                                                               |
|------------------------------------------|------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| Hasui<br>Kitahara<br>Fukushima<br>(1965) | Al <sub>2</sub> O <sub>3</sub><br>Mo<br>Ni alloy                                         | max. = 160<br>max. = 100<br>max. = 70                                                         |
| Fiszdon<br>Lesinski<br>(1975)            | WC<br>Al <sub>2</sub> O <sub>3</sub>                                                     | range = 30 to 130<br>{ mean $\hat{=}$ 80<br>range = 60 to 340<br>{ mean $\hat{=}$ 220         |
| Petrov<br>Morenov<br>(1967)              | Al <sub>2</sub> O <sub>3</sub><br>W                                                      | max. = 320<br>max. = 140                                                                      |
| Lemoine<br>Le Goff<br>(1969)             | Ni<br>C                                                                                  | range = 50 to 260<br>{ mean $\hat{=}$ 75<br>range $\hat{=}$ 80 to 280<br>{ mean $\hat{=}$ 110 |
| Fiszdon<br>(1979)                        | Al <sub>2</sub> O <sub>3</sub> (measured)<br>Al <sub>2</sub> O <sub>3</sub> (calculated) | range = 80 to 220<br>{ mean $\hat{=}$ 155<br>range = 130 to 250<br>{ mean $\hat{=}$ 200       |

the present work is not representative of typical plasma spraying processes. This large discrepancy in the results arises because there is no accurate description of the radiation emitted by a particle and the manner in which it is attenuated by the recording equipment.

The temperature measurements, unlike the exposure calculations, do not rely on the particle emissivity, if it is assumed that the emissivity is discrete and invariant to temperature and wavelength.

Thus it was noticed before that the response ratio-exposure curve is translated in the negative direction along the exposure axis as the emissivity is increased (Figure 3.22). However it can also be seen that the temperature calculation will not change under the same conditions because the absolute densities are also translated along the exposure axis (Figure 3.23). The temperature of the particle surface is measured in this work and these measurements (Table 3.9) show that the temperature of each mild steel particle generally decreases when moving away from the torch. The temperatures of those streaks that are not recorded in Table 3.9 and the positions shown as "off scale" were in excess of the boiling point of iron ( $3023^{\circ}\text{K}$ ). It is not possible for the same particle to vaporise and recondense under the conditions experienced within a plasma so the above results could be interpreted as ablation from the particle rim. However it is more probable that the calculations are in error because, as mentioned before, the various corrections for the radiation distributions emitted from the source are not completely known. Another anomaly is that the film response does not change progressively as would be expected for ideal particles that slow down and cool as they move away from the torch. For example no blue density value could be measured for streak 5 at positions 2 and 3 even though the red density was quite significant, and for streak 6 at position 4 no red density was measured although the blue density was high. Therefore it is apparent that the radiation of the blue and red wavelength ranges is not attenuated to the same degree and that the overall transmission factors are functions of both the plasma tail flame length and the optical system employed to gather and sense the radiation.

### 3.3.3 Conclusions

(1) Significant errors arise in the calculation of the particle temperature and relative velocity and these reduce the accuracy of the photo-thermographic technique and limit its application. In particular these errors include:

- (i) The particle emissivity is not known in relation to the wavelength of the radiation and the temperature.

This problem could be simplified by using an oxide material, such as alumina, which has a well characterised emissivity. It was also noticed from the streak patterns that the mild steel particles appeared to react in the plasma flame and this could explain an increase in the particle temperature when moving away from the torch. No reactions which complicate the thermal history of a particle would occur if alumina was used and additionally a greater temperature range could be examined since the melting point of alumina ( $2573^{\circ}\text{K}$ ) is greater than that of mild steel ( $2073^{\circ}\text{K}$ ).

(ii) The radiant intensity from point to point over the field of view must be corrected for the lens system employed. The manner in which the film density changed over the field of view could be examined by carrying out a series of density traces on the film and these corrections could then be incorporated into the response ratio calculations.

(iii) The total radiation intensity of a particle is altered by the plasma tail flame. Again a series of trials could be carried out on measuring the film density after exposure from the radiation of the plasma tail flame. Also the plasma tail flame could be blown away from the particles by a jet of air to minimise its exposure effect; but in this case the properties which are measured may not be typical of the plasma spraying process.

(2) The results of the film calibration (section 3.3.1) agree reasonably well with the theoretical calculations when it is considered that a large number of assumptions have been made in the absence of technical data.

(3) The results of the particle velocity and thermal histories (section 3.3.2) in general agree qualitatively to the simple theory that particles both cool and slow down as they move away from the torch nozzle. The results are limited by the errors listed in (1) above. Also there is no suitable standard (or model particle) which has been exposed for the same time that is equivalent to the length

analysed by the microdensitometer. Thus the microdensitometer was used on a setting which examined a length of  $0.825 \times 10^{-3}$  m and this area can represent exposure times of from  $10^{-4}$  to  $10^{-5}$  seconds which depend on the particle velocity. These exposure times are far less than the maximum speed of a between-the-lens shutter (1/400 second) and thus the theoretical calculations cannot be directly checked with a critical experiment.

(4) With the above shortcomings in mind it is considered that further extensions to the experimental work are not warranted because of :

- (i) the fundamental difficulty of obtaining a practical calibration exposure, and
- (ii) the limited results that are possible.

## CHAPTER FOUR

### CHARACTERISATION OF COATINGS

#### 4.1 INTRODUCTION

Maximum adhesion of a coating occurs when the particles arrive at the substrate in the fully molten condition so that they may flow onto the substrate surface to form a coherent layer. The physical state of the coating particles at their moment of impact and any interactions with the substrate can be determined by microscopy. Much work has previously been carried out on the metallography of coatings in relation to how the coating structure is controlled by plasma spraying variables such as particle size and distribution (Peterson, 1968, 1971; Andrews and Fuller, 1975), type of arc gas (Ingham and Fabel, 1975; Wellner et al., 1978), the plasma device used during the spraying procedure (Tucker, 1974), substrate surface topography (Safai and Herman, 1977; Apps, 1974a, 1974b) and the torch to substrate distance (Kumar and Das, 1978).

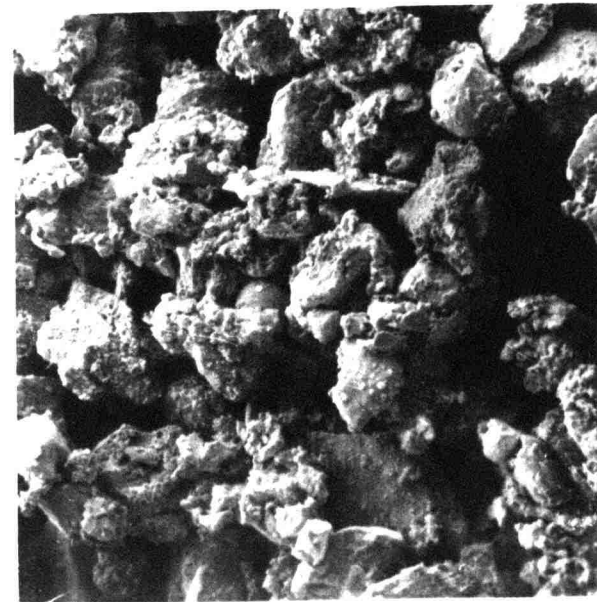
In this work a study of the coating surface and profile (cross-section perpendicular to the substrate surface) was initially carried out to characterise the deposit. Metal and ceramic deposits were produced and examined by optical microscopy and by scanning electron microscopy (SEM), and in some cases these were compared with coatings procured from industry.

Since this chapter examines the coating structure it is most appropriate to also include observations from the controlled fracture of specimens.

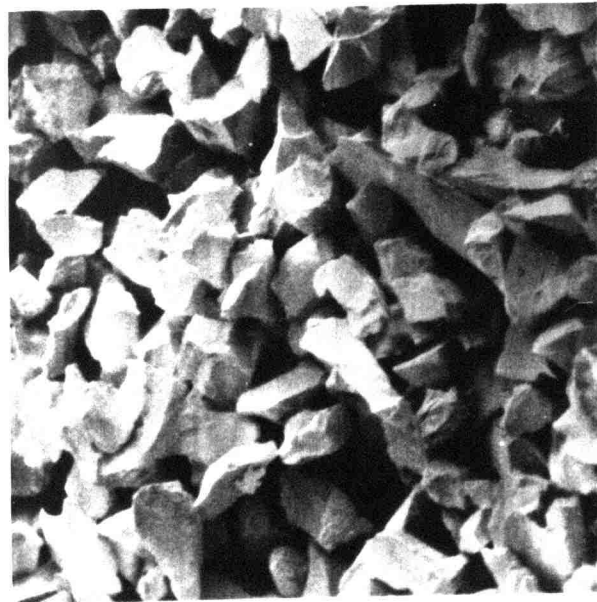


Table 4.1 (continued)

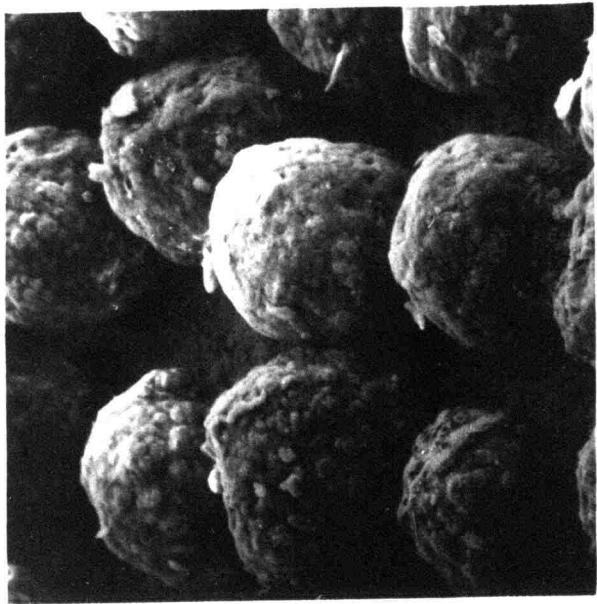
| (c) <u>Recommended Plasma Spraying Parameters</u>          |                |                   |                                   |                     |
|------------------------------------------------------------|----------------|-------------------|-----------------------------------|---------------------|
| (Gun-type Metco 3MB using argon and hydrogen gas mixtures) |                |                   |                                   |                     |
|                                                            |                | <u>Mild Steel</u> | <u>Nickel-Aluminium Composite</u> | <u>Grey Alumina</u> |
| Arc gas flow rate ( $\ell \text{ min}^{-1}$ )              | Ar             | 32                | 26                                | 32                  |
|                                                            | H <sub>2</sub> | 5                 | 5                                 | 5                   |
| Electrical characteristics                                 | Current (A)    | 400               | 500                               | 500                 |
|                                                            | Voltage (V)    | 70 - 80           | 65 - 70                           | 60 - 70             |
|                                                            | Power (kW)     | 28 - 32           | 32 - 35                           | 30 - 35             |
| Powder feed rate ( $\text{kg hr}^{-1}$ )                   |                | 4.6               | 4.1                               | 3.2                 |
| Deposition efficiency (%)                                  |                | 75                | 60                                | 80                  |
| Spray Distance (cm)                                        |                | 10 - 15           | 10 - 18                           | 5 - 10              |
| (d) <u>Recommended Flame Spraying Parameters</u>           |                |                   |                                   |                     |
| (Gun-type Metco 5P)                                        |                |                   |                                   |                     |
|                                                            |                | <u>Mild Steel</u> | <u>Nickel-Aluminium Composite</u> | <u>Grey Alumina</u> |
| Torch to substrate distance (cm)                           |                | 13 - 18           | 18 - 25                           | 5 - 8               |
| Oxygen flow rate ( $\ell \text{ min}^{-1}$ )               |                | 28                | 24                                | 28                  |
| Acetylene flow rate ( $\ell \text{ min}^{-1}$ )            |                | 15                | 14                                | 16                  |
| Power feed rate ( $\text{kg hr}^{-1}$ )                    |                | 5.9               | 4.6                               | 1.4                 |



(a) Mild Steel



(b) Grey Alumina



(c) Nickel-Aluminium.

Figure 4.1: Morphology of Feed Powders.

#### 4.2.2 Substrate Preparation

The substrate surface has a large effect on the coating adhesion (Apps, 1974a, 1974b; Bardal et al., 1973; Herpol and Tavernier, 1966 Epik et al., 1966) and these were prepared in the standard manner (BS4495, 1969; BS4761, 1971; BS4950, July 1973) by grit blasting with alumina (-1.59 to +0.58 mm) at a pressure of 0.15 to 4.00 MPa.

The grit shape is shown in Figure 4.2 and a grit blasted mild steel substrate is shown in Figure 4.3. Measurements of the surface roughness (Talysurf 4) for a number of grit blasted and flame sprayed substrates are shown in Table 4.2.

Table 4.2: Surface roughness of grit blasted and coated substrates

| Condition    | Material        | CLA ( $\mu\text{m}$ ) |
|--------------|-----------------|-----------------------|
| Grit blasted | Mild steel      | 7.1                   |
| Grit blasted | Brass           | 8.8                   |
| Grit blasted | Aluminium       | 8.8                   |
| Coated*      | Ni-Al composite | > 10.0                |
| Coated*      | Grey alumina    | 3.5                   |

\* Flame sprayed, according to conditions shown in Table 4.1(d), onto a grit blasted mild steel substrate.

#### 4.2.3 Production and Examination of Coatings

The samples were flame sprayed in the laboratory according to the schedules in Table 4.1d whereas the plasma sprayed samples obtained from industry were prepared under the conditions in Table 4.3.

Samples prepared for the controlled fracture experiments were plasma sprayed in the laboratory according to the conditions set out in Table 4.4. These coatings were incorporated into a test configuration where a loading fixture was bonded to the coating surface and then the assembly subjected to a tensile load. This method of testing is examined

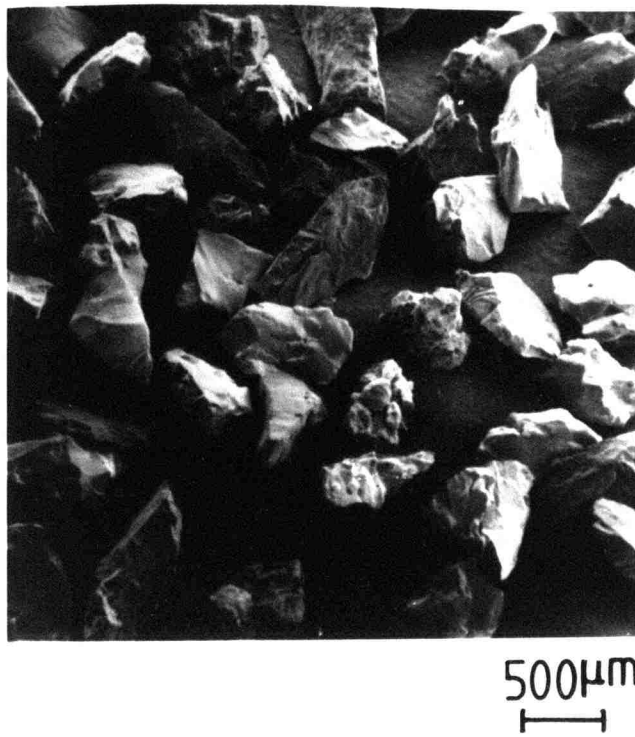


Figure 4.2: Morphology of alumina grit blasting medium.

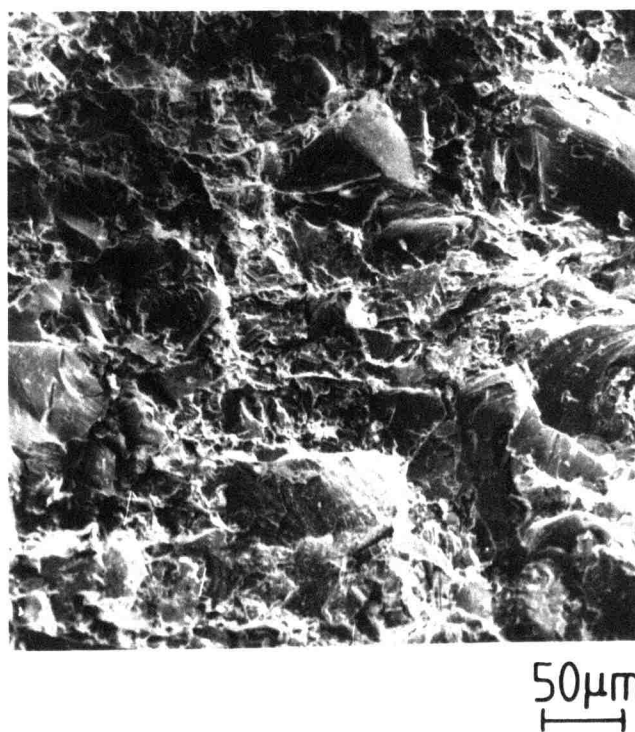


Figure 4.3: Morphology of mild steel substrate that has been grit blasted with alumina.

in chapter 5 and only details of the fracture appearance as they relate to coating structure are reported in this chapter. It should be pointed out that the tensile adhesion strength values were not typical of plasma sprayed coatings and thus they are not included in this work. However it is considered that the fracture surfaces of these samples are representative of the coating structure near the coating-substrate interface and within the coating.

Table 4.3: Plasma Spraying Schedule

| Coating Material                                       | Deposit Thickness (mm) | Gas Flow Rate ( $\ell \text{ min}^{-1}$ ) |    | Electrical Input |               |            |
|--------------------------------------------------------|------------------------|-------------------------------------------|----|------------------|---------------|------------|
|                                                        |                        | Ar                                        | He | Voltage (volt)   | Current (amp) | Power (kW) |
| Metco 450 (Ni-Al)                                      | 0.5 - 2.0              | 28                                        | -  | 43               | 412           | 18         |
| Metco 101 ( $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$ ) | 0.5                    | 28                                        | 7  | 51               | 600           | 31         |
| Metco 91 (Mild steel)                                  | 1.0                    | 28                                        | -  | 40               | 415           | 17         |

\* Spraying carried out with a Plasma-dyne SG-1B(S1) gun.

Table 4.4: Plasma Spraying Conditions of Samples produced for Controlled Fracture Experiments.

|                          |                            |
|--------------------------|----------------------------|
| $\text{N}_2$ flow rate   | $17 \ell \text{ min}^{-1}$ |
| Ar flow rate             | $7 \ell \text{ min}^{-1}$  |
| Voltage                  | 32 volts                   |
| Current                  | 217 amps                   |
| Power                    | 6.9 kW                     |
| Powder Feed Rate         | $10 \text{ kg hr}^{-1}$    |
| Torch-substrate distance | 15 cm                      |

The surface topography of the coating and, in some cases, sections perpendicular to the substrate were examined by SEM after the appropriate precautions against specimen charging had been taken.

Taper sections ( $45^{\circ}$ ) of the coating profiles were also produced for metallographic examination by mounting in bakelite and polishing in the usual manner. These samples were placed within brass tubing to prevent preferential abrasion of the coating and they enabled the "splat" appearance of the coating to be distinguished together with oxide boundaries and porosity. The smooth surface of metallographic specimens also permitted X-ray analysis for a qualitative description of elemental distribution within the coating and at the coating-substrate interface.

### 4.3 RESULTS

#### 4.3.1 Metal Coatings

The plasma sprayed mild steel and nickel-aluminium coatings had similar morphological features as can be expected from their particle size distribution and recommended spraying conditions. These features are shown for the Ni-Al composite coating in Figure 4.4 where particles have reached the substrate surface in the molten condition and spread out. Some areas appear white due to charging of particles and show those particles which have reacted to produce oxides. The particles also exhibit pinholes which are characteristic of porosity due to evolution of absorbed gases.

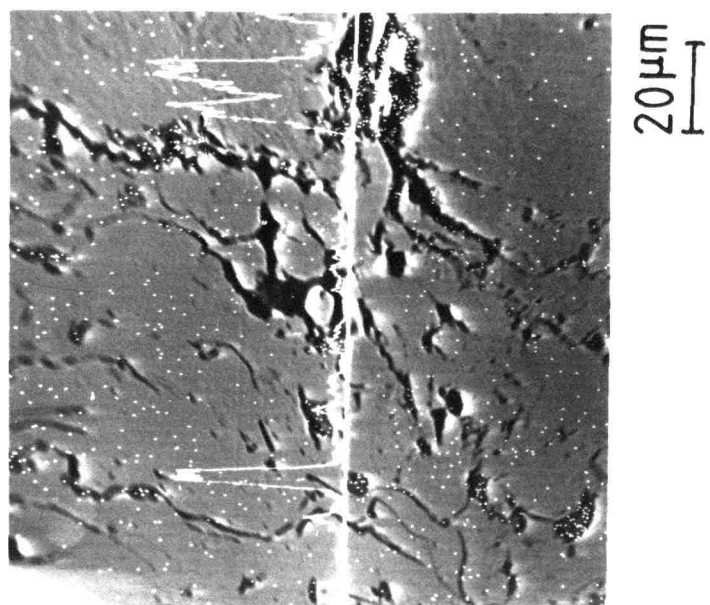
Figure 4.5 shows X-ray element line scans and X-ray maps, prepared using the SEM, across the interface between the coating and substrate. Only a small amount of aluminium was detected in the coatings and this was unalloyed with the nickel (or iron) but present at the particle boundaries presumably as an oxide. Some large areas high in aluminium were also detected at the interface and were found to be alumina grit which embedded into the substrate during the surface preparation. The microstructure shows that some of the metallic particles have extensively deformed to give a saucer shaped deposit firmly attached to the substrate while other regions of the coating pulled away from the substrate. The regions of separation at the interface were associated with oxides which support the theory that these are detrimental to coating adhesion.

Dark areas could also be distinguished within the body of the coating which were shown to be either high or low in aluminium (Figure 4.5a). The aluminium deficiency can result from the polishing operation when oxides pull out from around the particle or it can be an area of porosity within the coating. Porosity can be present either between lamellae of particles (interlamellae) or within particles (internal) and it is not clear what form is present in the examination of Figure 4.5, although internal porosity has already been observed (Figure 4.4) for Ni-Al coatings.

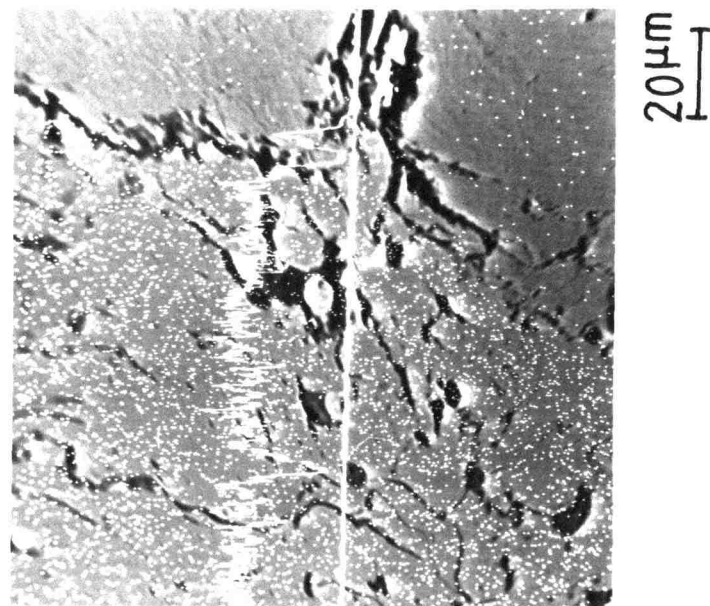
The fracture surfaces of mild steel coatings also exhibited particles which had flattened to a saucer shape on impact with the substrate. Figures 4.6 and 4.7 show the micro-structure of particles which were in direct contact with the substrate. Dendrites were observed on the particle surface (Figure 4.6) which were associated



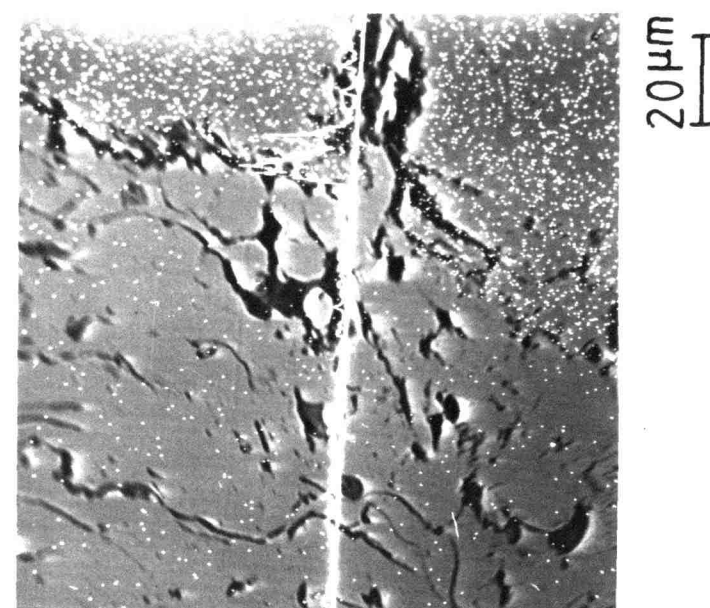
Figure 4.4: Surface of a Ni-Al composite coating.



(a) Al



(b) Ni



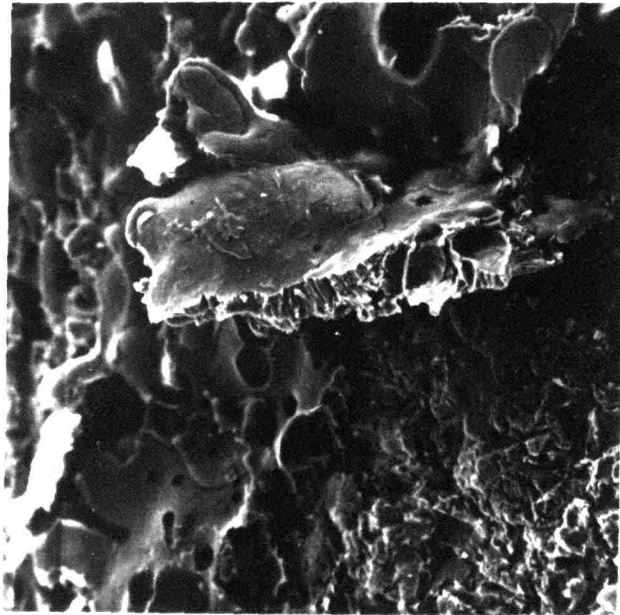
(c) Fe

Figure 4.5: X-ray line scans and X-ray maps of nickel-aluminium coated onto a grit blasted mild steel substrate.



5 μm

Figure 4.6: Fracture surface of mild steel plasma sprayed onto a mild steel substrate. Note micro-cracks and dendrite artefacts.



20 μm

(a) Plastic deformation of particle.



2 μm

(b) Columnar grain growth within particle.

Figure 4.7: Fracture surface of mild steel plasma sprayed onto a mild steel substrate.

with random crystal nucleation and growth whereas columnar grain growth approximately perpendicular to the substrate surface was distinguished (Figure 4.7) for other particles. In the former case the deposit particle has not undergone any discernable deformation and microcracks are present which may have arisen during the formation of the coating (from shrinkage or impact by other particles) or result from the tensile adhesion test.

On the other hand the particle exhibiting columnar grain growth has separated from the substrate and deformed plastically, which suggests that good thermal contact of the particle with the substrate (which thus produces columnar grain growth) may not necessarily imply good mechanical keying and good adhesion. Thus the solidified particle may separate from the substrate after shrinkage or interaction with overlaying particles.

#### 4.3.2 Ceramic Coatings

The plasma sprayed alumina coatings essentially exhibited the same features as the metal coatings except that some particles were only spheroidised and did not flow at the substrate surface. Internal porosity was distinguished in some particles by spot-like features on the surface (Figure 4.8). The inter-lamellar surfaces revealed by fracture of these coatings were generally very smooth with little evidence of the crystal growth pattern. Some of the particles however, like the metal coatings, showed a dendritic pattern (Figure 4.9) which implies a random orientation of the crystals and nucleation throughout the droplet. On the other hand some fractured lamellae (Figure 4.10) revealed a fine columnar growth pattern consistent with nucleation and rapid growth from the region in contact with underlying material. This would be expected if there was efficient heat transfer from the flattened droplet in intimate contact with the underlying solid.

In general a large number of fine particles were observed on the surface of ceramic coatings and these were probably the lower size fraction of the powders. The coating profile (Figure 4.10) shows

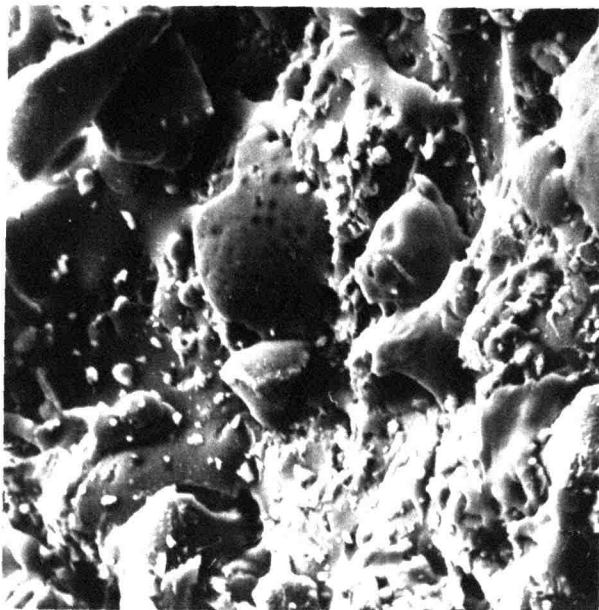


Figure 4.8: Alumina plasma sprayed onto a mild steel substrate. View of surface.

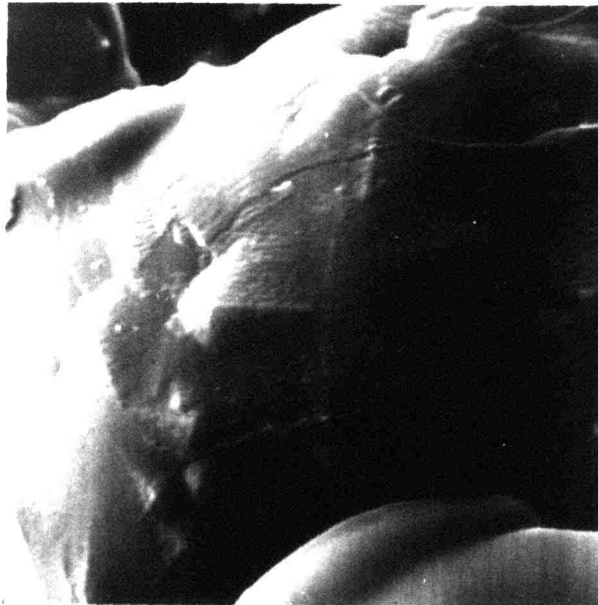


Figure 4.9: Dendrites exhibited on the surface of a plasma sprayed alumina particle.

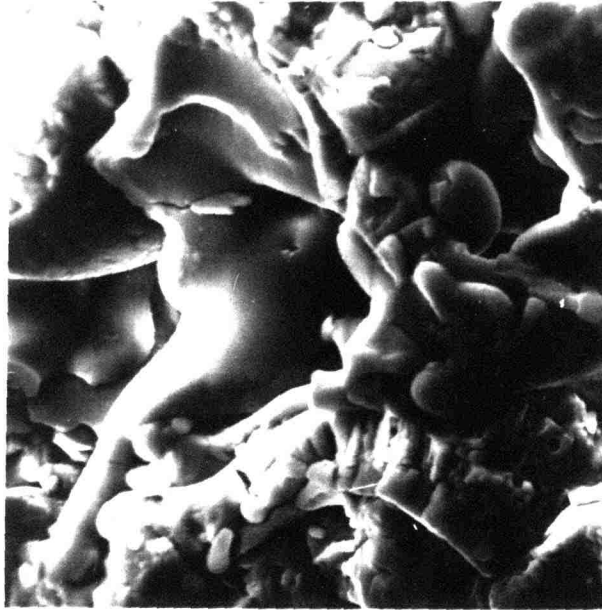


Figure 4.10: Profile of a plasma sprayed alumina coating. Mild steel substrate is not shown but on the left-hand edge of the figure.

particles which have the characteristic saucer shape and some which have been spheroidised in the plasma flame but have not deformed appreciably on impact. Sites can be distinguished between particles where continuous, very fine interlamellar porosity would be prevalent (formed by imperfect bonding between adjacent lamellae) in contrast to voids within particles arising from gas evolution (internal porosity).

The scanning electron micrographs of the polished coating profiles of the alumina coating (Metco 101) exhibited dark and light areas (Figure 4.11) which on X-ray analysis were distinguished as alumina and titania respectively (Figure 4.12). The background of the X-ray maps is poorly resolved since the lens current has been adjusted for a large X-ray count rate. The alumina and titania particles can be differentiated from their contrast because the secondary electron emission is dependent on the atomic number. The white areas in Figures 4.11 and 4.12 result from specimen charging in the electron microscope and show where epoxy adhesive has penetrated between the coating and substrate. Other regions of the coating have a fine granular structure around the particle boundaries arising from the polishing operation.

#### 4.4 DISCUSSION

The coating structures examined in this work are representative of those that have been reported in the literature. The structure of nickel-aluminium composite coatings has been investigated extensively because of their unique property of good adhesion to a surface which may not have been grit blasted. It has also been established that ceramic coatings adhere more strongly to these composite coatings than to the grit blasted substrate, so that it is common thermal spraying practice to use such a metal interlayer during the preparation of a coating. The interlayer is termed a 'bond coating' and the most suitable materials are based on Ni-Al, Ni-Cr and Mo. It is important to note that Ni-Al and Ni-Cr powders are not mixtures of

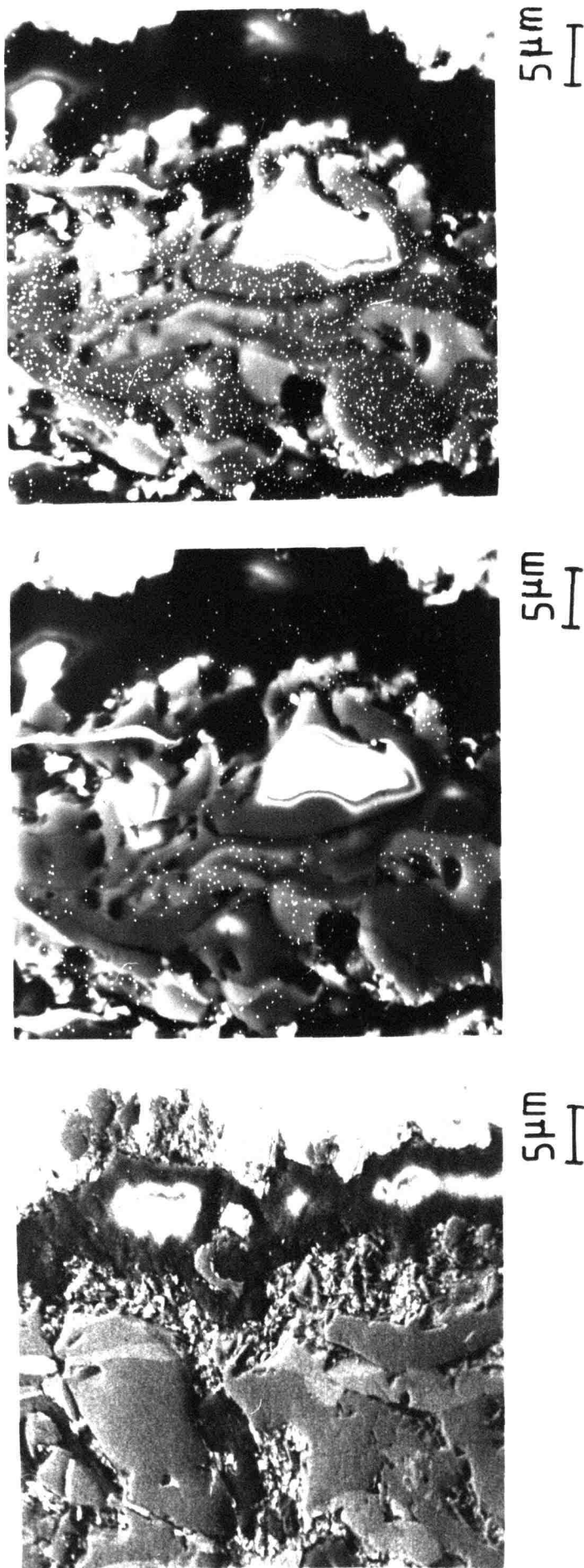
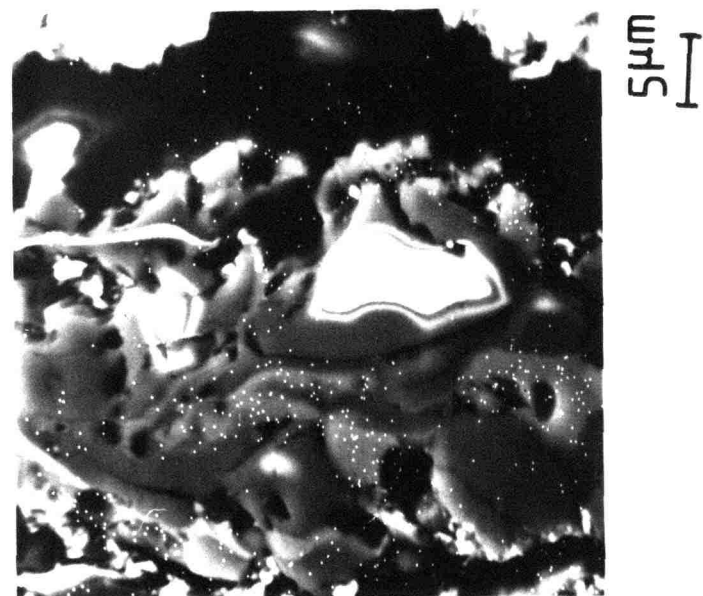
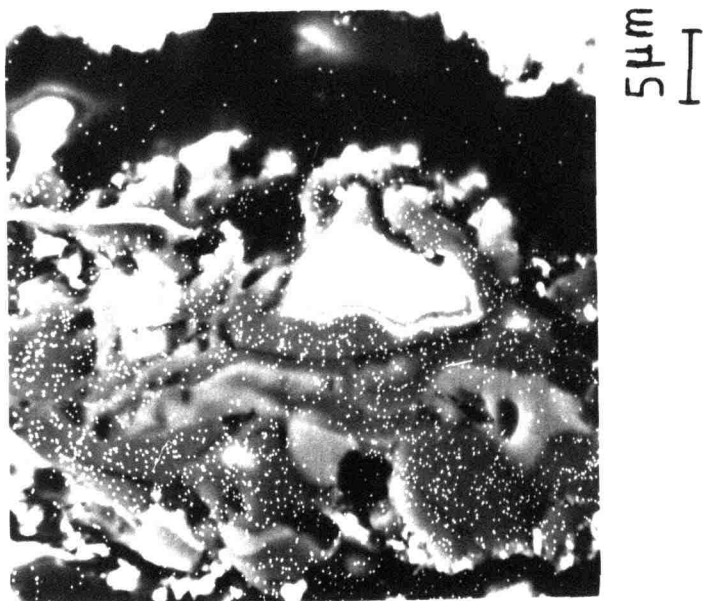


Figure 4.11: Profile of alumina plasma sprayed onto a grit blasted mild steel substrate (right-hand edge of figure.)



(a) Ti map



(b) Al map

Figure 4.12: X-ray maps of a plasma sprayed alumina coating. View is of the coating profile with the grit blasted mild steel substrate on the right-hand edge of the figure.

the individual constituents but are composite powders consisting of a core material encased in the other component (Longo, 1966, 1967a, 1967b; Dittrich and Sheppard, 1969; Houben and Zaat, 1974b).

There has been much discussion concerning the adhesion mechanism of bond coatings and it appears that some metallurgical bonding by chemical reaction occurs with the substrate. The high temperature prerequisite for alloying at the substrate surface arises from the chemical reaction of the powder constituents and this behaviour has been verified (Dittrich, 1965; Longo, 1966; Kudinov et al., 1975) by observing an increase in the particle brightness during its time of flight. Gases are liberated during this reaction and may form the internal porosity that was observed within the coatings (Figure 4.4). This mechanism cannot be used to account for the high adhesion strength of molybdenum coatings; however it has been observed (Allsop et al., 1961; Matting and Steffens, 1963; Gerdeman and Hecht, 1972, p.29) that molybdenum reacts with the substrate and with steel, for example, forms a Mo-Fe intermetallic which can be distinguished by optical microscopy (Kampmann and Kirner, 1972).

The Metco 101 coatings exhibited the characteristic lamellar structure which revealed individual alumina and titania particles. It has been suggested that the first particles to be deposited cool most rapidly ( $10^4$  to  $10^6$  °C sec<sup>-1</sup>) and form an amorphous layer (Safai and Herman, 1978; Wilms and Herman, 1976) which has good mechanical contact with the substrate. Subsequent layers have a lower cooling rate because they are thermally insulated from the substrate by the amorphous layer and as well the thermal gradient is less since the coating surface has been heated up to about 600°C. Thick coatings (> 250 µm) exhibit columnar grain growth perpendicular to the substrate surface because of the slow cooling and thus the grain size increases with the coating thickness. Metal coatings on the other hand (Safai and Herman, 1977) exhibit a change in grain orientation which is dependent on the anisotropic heat extraction throughout the impinging particle. In the core region of the particle, which comes into initial contact with the substrate, heat is extracted through the substrate whereas in the peripheral area heat is extracted via the core region and the grains are thus radially orientated from the core.

The material used in this work (Metco 101) consists of a mixture of alumina and titania powders. Other  $\text{Al}_2\text{O}_3$  -  $\text{TiO}_2$  powders are available commercially (Safai and Herman, 1978) and consist of either sub-micron titania particles which completely surround and adhere to the alumina particles (termed composite powders) or are produced as a powder which has been pre-reacted to form a mixture of  $\alpha\text{-Al}_2\text{O}_3$  and  $\beta\text{-Al}_2\text{O}_3\cdot\text{TiO}_2$  (termed fused powders). The purpose of adding a second phase to alumina is to increase the density and tensile bond strength of the coating., (Durmann and Longo, 1969; Safai and Herman, 1978; Wilms and Herman, 1976) however the mechanism by which this occurs is not understood.

Scanning electron micrographs of the coating profile (Figure 4.11) show that titania particles have deformed to a greater extent than the alumina. This would be expected from the lower melting point of  $\text{TiO}_2$  (1830 to 1850°C compared to that of  $\text{Al}_2\text{O}_3$  which is  $2015 \pm 15^\circ\text{C}$ ), even though the kinematic viscosity of alumina (Elyutin et al., 1969, 1972) just above its melting point is similar to that of titania (Mitin and Nagibin, 1971) as shown in Figure 4.13.

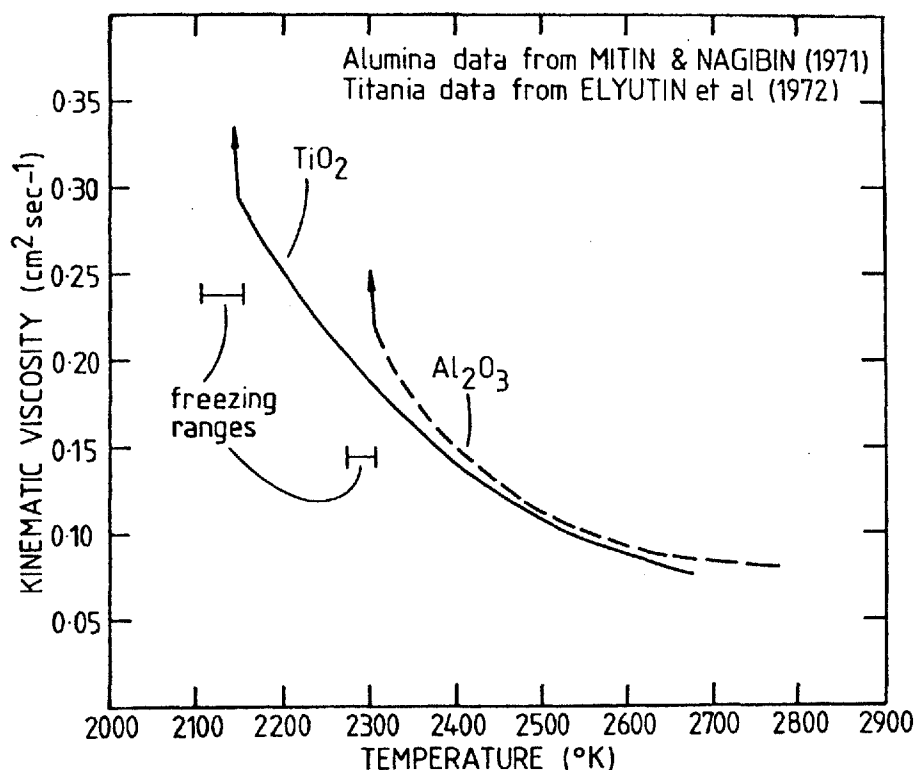


Figure 4.13: Kinematic viscosities of alumina and titania with respect to temperature.

Thus the kinematic viscosity of titania at its melting point is less than that of alumina at the same temperature and may extend the relative solidification time of the titania so that it flows around the prior solidified alumina. However it should be considered that equilibrium conditions are not attained during the splat cooling process of plasma spraying so it is unlikely that relatively small changes in the temperature-kinematic viscosity behaviour of individual components will have any discernable effect on the coating structure.

What may be the more important parameter to examine is the wetting angle between the individual components of the powder. No data can be found on the wetting angle between alumina and titania but Mitin and Levin (1968) present data (Table 4.5) on the contact angles of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  on some high melting metals. This suggests that there is a strong possibility that  $\text{TiO}_2$  will flow around  $\text{Al}_2\text{O}_3$  particles to produce a dense deposit.

Table 4.5: Contact angles of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  on some high melting point metals.

|                         | $^{\circ}\text{C}$ | W | Mo | Ta | Nb |
|-------------------------|--------------------|---|----|----|----|
| $\text{Al}_2\text{O}_3$ | 2080               | 7 | 15 | 28 | 40 |
| $\text{TiO}_2$          | 1800               | 0 | 0  | 0  | 0  |

Cavities and pores are formed between the individual particles in the sprayed coatings because interparticle diffusion is limited and particle flow is hindered during the splat cooling process. Internal porosity can arise from (Meyer, 1964; Koubeck, 1970):-

- (i) gases adsorbed by the particle in the plasma effluent may desorb when the particle solidifies;
- (ii) the particles may become superheated in the plasma and vaporise ( $2980 \pm 60^{\circ}\text{C}$  for alumina and 2500 to  $3000^{\circ}\text{C}$  for titania); or

- (iii) metal oxides may partially convert to nitrides in the nitrogen plasma which may subsequently decompose and evolve nitrogen when they come into contact with oxygen in the air.

This work did not establish how the internal porosity was formed in the alumina coatings.

#### 4.5 CONCLUSIONS

The ceramic coatings exhibited similar morphological features to the metal coatings in the form of flattened particles, dendritic artefacts on the particle surface, a columnar crystal structure and porosity of various forms.

The columnar structure that was observed in some flattened particles can be explained by assuming efficient heat extraction through the underlying structure (substrate or coating). In a similar manner the dendritic artefacts would be expected to preferentially nucleate on the surfaces of large particles.

In general the microstructures were similar to previously reported work and provide no new insights into the properties of these coatings and the relationship between adhesion and structure. These studies were primarily aimed at determining coating structure, and the relationship of these with adhesion will be discussed further in Chapters 5 and 6.

## CHAPTER FIVE

### REVIEW OF ADHESION MEASUREMENTS ON COATINGS

#### 5.1 INTRODUCTION

A major requirement of any coating is that the adhesion to the substrate is sufficient to maintain its integrity during use and the measurement of coating adhesion is therefore of major practical importance. Several reviews have already been written on the subject of adhesion measurement (Davies and Whittaker, 1967; Jacobsson, 1976; Mittal, 1976; Kretzschmar, 1977; Böhme, 1978) but the emphasis in this thesis concerns specific testing methods to determine the adhesion of plasma and flame sprayed coatings. This chapter critically examines the relationship between data derived from adhesion measurements and the coating structure to the mechanism of adhesion.

It is concluded that although existing adhesion tests may provide quality control data, they provide little information concerning the service failure of coatings or the mechanism of adhesion. Indeed a fracture toughness criterion, similar to that which is normally applied for the acceptability of an adhesive, may be more applicable for the case of flame and plasma sprayed coatings and this approach is developed further in Chapter 6.

## 5.2 MECHANISMS OF ADHESION

Possible mechanisms for the adhesion of plasma and flame sprayed coatings have been reviewed by Matting and Steffens (1963, 1967) and are summarised below.

### 1. Mechanical Keying

Mechanical keying results from the deposit material flowing round roughness peaks and into undercut regions of the substrate surface. This mode of adhesion explains the experimental observation that materials deposited onto polished substrates do not exhibit a high degree of adhesion; whereas the adhesion of the coating is markedly improved if the substrate is roughened. The model has shortcomings because there is no explanation for adhesion of bond coatings to smooth and unprepared substrates.

### 2. Physical Adhesion by Dispersion Forces

When two materials come into close contact some mutual attraction may be expected resulting from van der Waals' forces. This mechanism presupposes that the materials in contact are only one lattice spacing distant from each other and also that the deposit material wets the substrate. Dispersion, or van der Waals' forces, predict the highest adhesive strengths. It would be expected that since the materials have a high thermal energy content, the temperature conditions at the interface would play a major role in the adhesion of the deposit. Dispersion forces, however, do not depend on temperature and adhesion by van der Waals' forces takes place athermally.

### 3. Chemisorption and Epitaxy

Chemisorption and epitaxy, applied to plasma and flame spraying, concerns the oriented growth of the liquid onto the substrate. A surface roughening operation would be expected to greatly reduce the energy barrier which must be surmounted for orientated growth to occur because of the zones of high elastic lattice energy which are formed. At the same time macroscopic regions of orientated growth are unlikely because of the geometry of the substrate surface. The epitaxial growth

of crystals is therefore expected to occur on a microscopic scale and there has been some confirmation of this from electron microscope studies.

#### 4. Diffusion

If a metal is sprayed onto a metal substrate of the same material it is likely that self-diffusion will result. Also heated regions of plastically deformed areas of the substrate can recrystallise after contact with the sprayed particles and such zones are generally only a few microns deep. Since the substrate has a high defect concentration due to cold working and the splat cooled deposit material a high vacancy concentration, equivalent to that at high temperatures, the diffusion coefficients of both materials would be expected to be greatly increased and enhanced interdiffusion could be expected.

#### 5. Reaction

An intermediate phase may be produced simultaneously with diffusion. For example  $\text{Fe}_7\text{Mo}_6$  is formed at the high energy roughness peaks of a mild steel substrate when sprayed with molybdenum. Another example is the formation of intermetallic phases ( $\text{Fe}_3\text{Al}$ ,  $\text{FeAl}$ ) at the interface when aluminium is sprayed onto steel.

None of these models would be universally applicable to all examples of coating adhesion. It is most likely that a unified model would incorporate contributions from all of these possible mechanisms to a degree which depended on the specific example of coating-coating, or coating-substrate adhesion.

A major reason for the controversy concerning the adhesion of a coating is the lack of information regarding the particle temperature and velocity on impact with the substrate. Attempts have been made to rationalise these processes according to principles of heat and mass transfer reactions (Mash et al., 1961; Marynowski et al., 1965; Scott and Cannell, 1967; Okada and Maruo, 1968; Nachman and Gheorghiu, 1969; Fisher, 1972; Waldie, 1972; Rykalin and Kudinov, 1976; Sayce, 1976), but as it has already been pointed out in Chapter 3,

results from these measurements and calculations must be examined with care.

### 5.3 STANDARD METHODS FOR PREPARATION OF SUBSTRATES

Recommendations and standards which relate to the deposition of coatings are detailed in three British Standards (BS4495:1969; BS4761:1971; BS4950:July 1973). The generic term "flame spraying" in these Standards refer to, "... such processes as combustion gas flame, electric arc, plasma arc and detonation processes". The Standards pay particular attention to the surface preparation of the substrate. The surface "... should be sufficiently roughened to allow the coating to be bonded to the contour of the surface of the base material". Recommended methods are:

1. Grit blast preparation using crushed aluminium oxide of mesh size -16 to +44.
2. Machine preparation by rough threading or grinding.
3. Bond coating. This is the application of a flame sprayed interlayer of a metal or alloy which has good adhesion to the substrate, e.g. (Mo or Ni-Al).
4. A combination of the above. That is 2 followed by 1, 1 followed by 3 or 2 followed by 3.

The interlayer or bond coating may increase the adhesion strength of the resultant coating by reducing stresses in the coating which are caused by thermal expansion differences of the coating relative to the substrate material. Thermal stresses between the deposit and substrate can also be reduced by preheating the substrate to between 100-200°C immediately prior to deposition. Local over-heating of the substrate during deposition can be controlled by directing jets of compressed air onto the surface during spraying; a controlled cooling rate of the component after spraying will reduce thermal stresses. The bond coating in some cases may also reduce the

risk of coating failure due to corrosion or oxidation of the substrate surface.

#### 5.4 TESTS FOR MEASURING THE ADHESION OF A COATING

##### 5.4.1 Standard Methods of Tensile Tests

The adhesion of a plasma sprayed coating to a substrate is the principle property that determines its usefulness and application. The coatings are usually tested in a manner similar to that described by the ASTM Standard C633-69.

The test initially consists of thermal coating one face of the substrate and then bonding a loading fixture to the coating with a suitable adhesive. The coating is then trepanned around the base of the loading fixture so that shear stresses are avoided during the following tensile test of the assembly (Figure 5.1). The test is usually carried out at ambient temperature since higher temperature testing is restricted by the need for a suitable adhesive. The coatings must be applied in thicknesses greater than 0.38 mm since below this thickness the adhesive can penetrate to the substrate. Recommended strain rates during tensile testing are 0.013 to 0.021 mm sec<sup>-1</sup>.

The mode of coating failure (Figure 5.2) can be described as either adhesive or cohesive (Apps, 1974a, 1974b). Adhesive failure takes place when the entire coating separates from the substrate whereas failure occurs entirely within the coating for cohesive failure. True adhesive failure (also termed interfacial failure) rarely occurs because of the rough nature of the substrate surface and adhesive failure in this case is defined as taking place near to the interface where the fracture surface exhibits areas devoid of the coating. The strength is found from the simple relation:

$$\sigma = \frac{P}{A} \quad \dots (5.1)$$

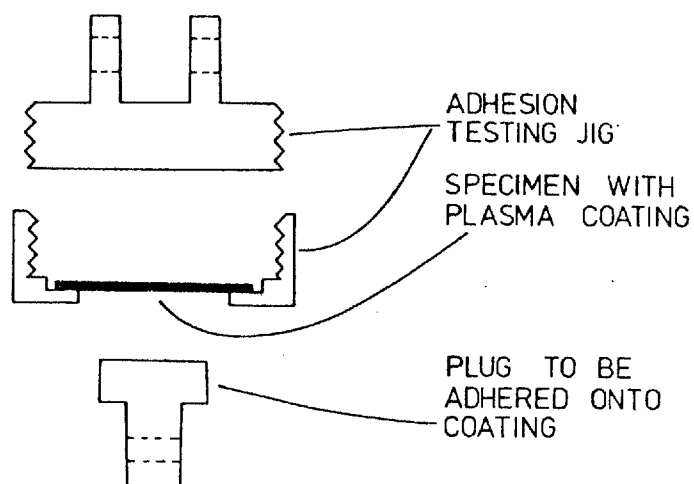


Figure 5.1: Tensile adhesion test (or bond strength test) of coatings.

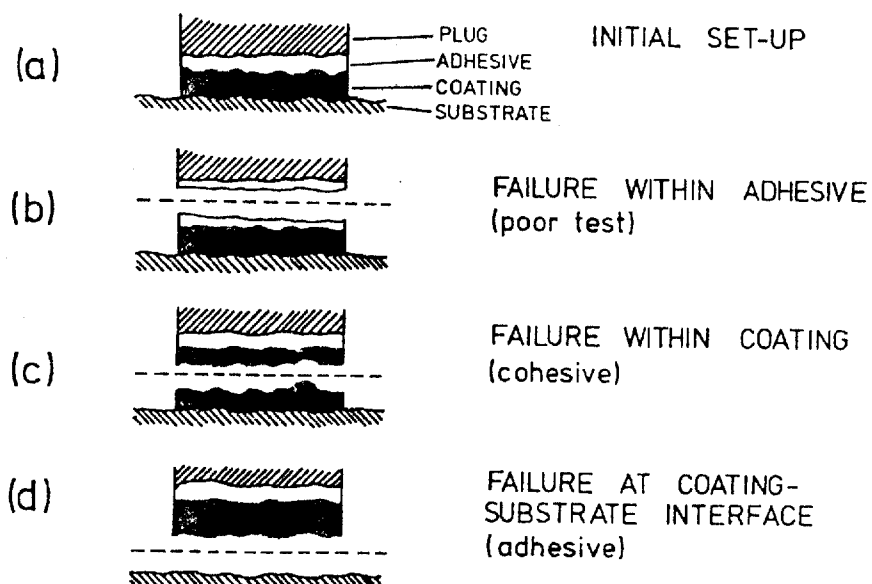


Figure 5.2: Modes of coating failure.

where  $\sigma$  = cohesive or adhesive strength (Pa)

P = force at failure (N)

A = cross sectional area of trepanned base ( $\text{m}^2$ )

Many other techniques (Mittal, 1976; Böhme, 1978; Jacobsson, 1976; Kretzschmar, 1977; Davies and Whittaker, 1967) have been devised which are based on this method of testing a coating; and they all suffer from a variety of disadvantages.

- (1) If failure occurs within the adhesive only the area within the coating is considered in the calculation to find the stress at failure (Böhme, 1978). This method is inaccurate because the test result has indicated either defective bonding of the sample or non-normal loading of the sample.
- (2) The manner in which the coating is loaded is not typical of stresses observed during the service life of a coating (Böhme, 1978).
- (3) The value of the measurements is influenced by the symmetry of the experimental set up and by the penetration of epoxy into pores of the coating (Catherall and Kortegas, 1972; Bardal et al., 1973; Hermanek, 1978).
- (4) The adhesive that is used to attach the plug to the coating must have a greater tensile strength than the coating. These adhesives are not readily available and have a limited shelf life (Minnesota Mining and Manufacturing, no date).
- (5) The elevated curing temperature of the adhesive may affect the adhesion of the coating since the residual stress distribution (Marynowski et al., 1965) may be altered.
- (6) The fracture surface of a test specimen normally exhibits both adhesive and cohesive failure. The tensile adhesion test only finds an average value when both of these failure modes act together and does not establish which failure mode limits the strength of the coating.

(7) The mechanism by which the coating structure contributes towards the adhesion is not readily ascertained without a quantitative assessment of the various modes of adhesion. The tensile adhesion test does not readily permit such mechanistic studies.

(8) Flaws in the form of micro-cracks, porosity and second phase inclusions within the coating will affect the adhesion of the coating. The role of these microstructural features of the coating cannot be examined by the tensile adhesion test.

However the tensile adhesion test is relatively simple to carry out and is useful in quality control and for providing a ranking of various types of coatings (Mock, 1966; Westerholm et al. 1961; Gerdeman and Hecht, 1972, pp. 52-59).

#### 5.4.2 Non-Standard Methods for Tensile Tests

Other tensile methods have been described (Sharivker, 1967; Lyashenko et al., 1969; Vadivasov et al., 1970; Zakharov et al., 1970) where a metal plug is pulled from underneath the deposit, Figure 5.3. In the first case (Figure 5.3a) the coating is subjected simultaneously to peeling and shearing. A major disadvantage of the method is that the specimen and disc are coated together when assembled so that the particles tend to enter the clearance between these two components and thus affect the rupture load. Also non-uniform heating of the specimen and the ring during deposition generates additional stresses in the deposit which also introduce errors in the evaluation of the rupture load. Equation 5.2 was proposed by Sharivker (1967) to find the "real strength of adhesion" ( $P_o$ ), which is defined as the value of adhesion strength if the specimen is unaffected by internal stresses, viz:

$$\tau = \mu(P + P_o) \quad \dots (5.2)$$

where  $\tau$  = shear stress on coating (Pa)

$P$  = external pressure (Pa)

$\mu$  = true coefficient of friction.

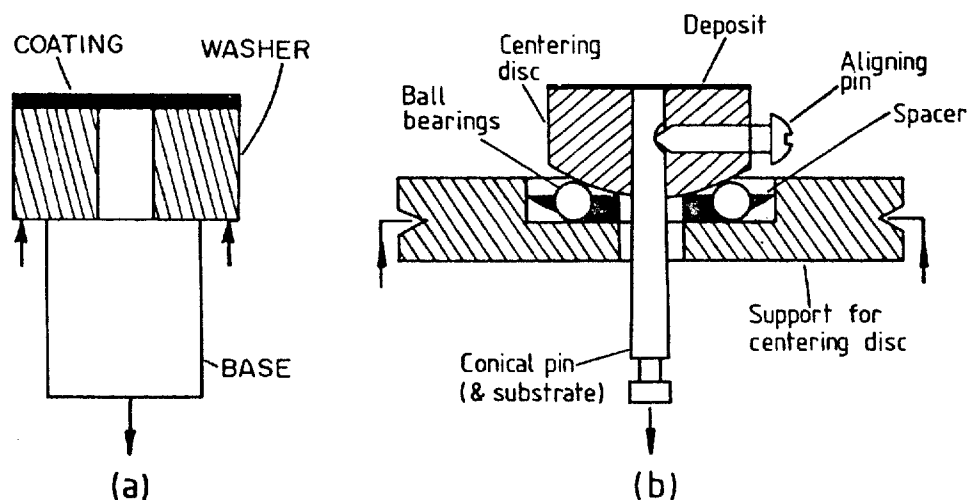


Figure 5.3: (a) Specimen for determining strength of adhesion (Sharivker, 1967).  
 (b) Centering device and specimen in cross-section (Lyashenko et al., 1969).

The method was improved (Lyashenko et al., 1969) by using a conical pin made of the experimental base material (Figure 5.3b). In this way the effect of friction between the pin and disc was eliminated and at the same time the gap between those parts reduced to a minimum.

Another method of evaluating the coating adhesion on the substrate has been described by Stanton (1974). The main requirement of this work was to devise a tension test that did not require the application of an adhesive plug to the deposit. The component parts required for each test included a test specimen, a pull-off bar and a threaded tie bar (Figure 5.4).

A cone of  $90^\circ$  inclusive angle was machined at one end of a 25.4 mm diameter bar to form the testing surface, and a similar one of  $60^\circ$  machined at one end of the pull-off bar. Both of these tapered ends were faced off to 9 mm diameter in order to provide registering faces and to ensure true axial alignment of the assembly when clamped together with the tie bar. The specimen surface (the surface of the  $90^\circ$  cone) could then be prepared by grit blasting. To

ensure that failure occurred at this face, the pull-off bar surface was prepared for 30 mm of its length. A coating of depth 0.25 to 0.35 mm was applied normal to the test surface while the whole assembly was rotated at a constant speed. The coned portion of the assembly and the prepared section of the pull-off bar were brought to a diameter greater than the original bar diameter by depositing a low shrinkage metal. After cooling the tie bar could be removed and the specimen subjected to a tension test.

Very little scatter of the experimental results was found for a considerable number of tests, but the problem of having to resolve the shear component of the force remains if the test is to be quantitative. It has been noted (Atkins, 1974) that the deposition technique makes it difficult to maintain the spraying angle perpendicular to the test surface and at the same time establish sufficient adhesion of the deposit material to the pull-off bar. This is because the coned portion of the pull-off bar is nearly parallel to the spraying direction and failure would be expected to occur in the abutting region of the test and pull-off bars and thus invalidate the test.

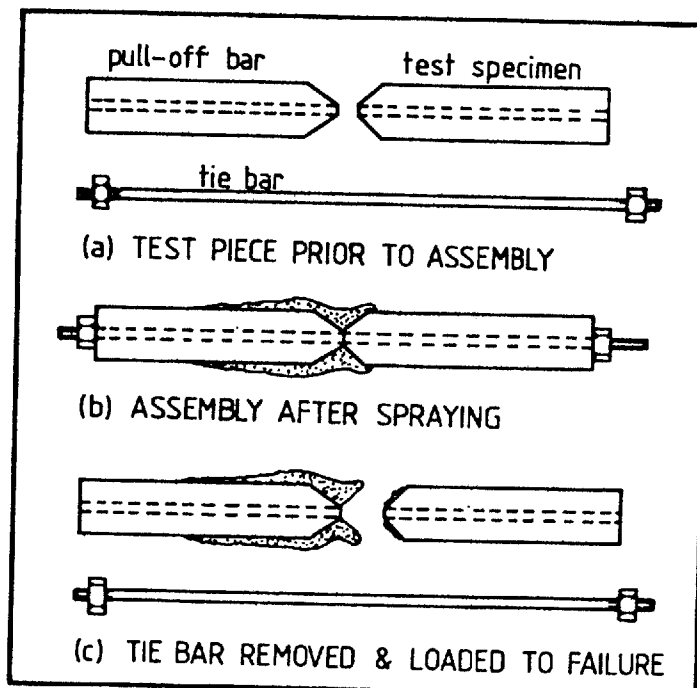


Figure 5.4: Adhesion testpiece (Stanton, 1974).

### 5.4.3 Shear Strength of Coatings

Figure 5.5 shows some experimental arrangements that have been used to carry out shear tests. For example Figure 5.5(a) and (b) shows how bushings transmit a shear load applied perpendicular to the specimen surface. The stripping force causes the deposit particles to slide over the substrate surface so that an additional frictional force must be overcome. If the frictional force exceeds that of particle adhesion then the rupture of the deposit will appear to have a cohesive component. The results of the shear test are strongly affected by the machining of the test assembly because a certain clearance must be provided between the specimen and the bushings. A method, Figure 5.5(c) to (d), devised by Suhara et al. (1974) does not suffer from these problems. In this example tungsten wire was explosion sprayed onto mild steel and both;

- (i) the shearing strength, and
- (ii) the critical shearing stress;

of adhesion of the coating on the substrate were found by changing the mode of the principal shearing force.

### 5.4.4 Shear Strength of Particles

Rykalin and Kudinov (1976) used an instrument (Figure 5.6) to shear single particles from the substrate surface and considered that adhesion to the substrate arose from interactions across the particle substrate interface. A "strength of growth rate constant" (K) for particle cohesion was defined as:

$$K = -\frac{1}{t} \ln\left(1 - \frac{N(t)}{N_0}\right) \quad \dots (5.3)$$

where  $t$  = the interaction time (sec)

$N(t)$  = the number of atoms that react during the interaction time.

$N_0$  = the number of atoms in the particle and substrate that are in contact.

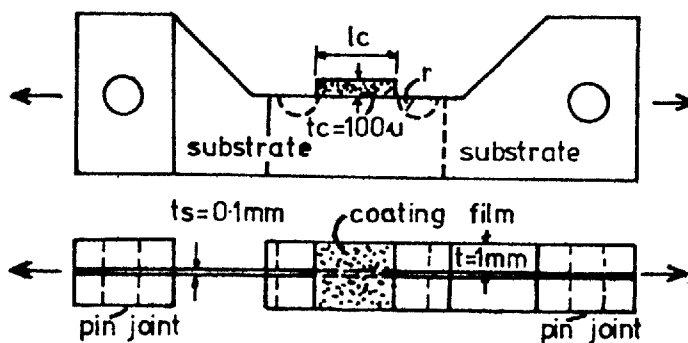
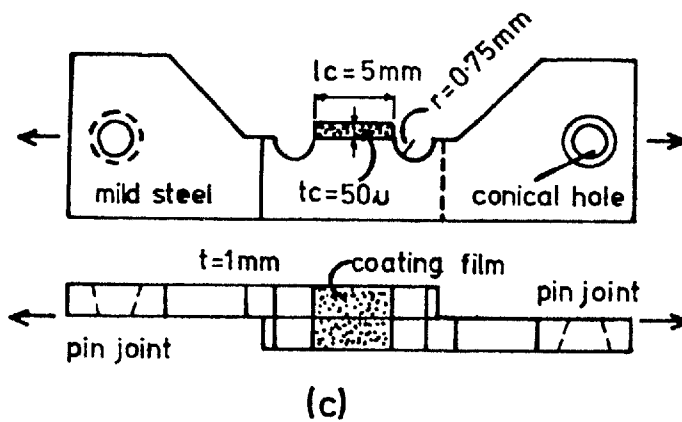
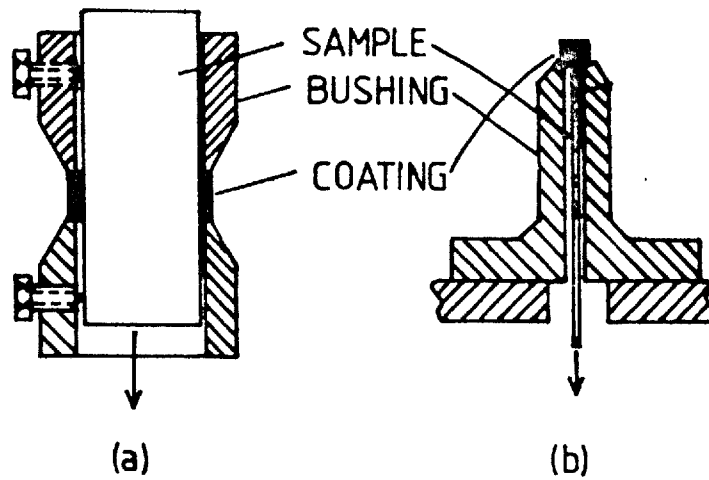


Figure 5.5: Specimens for shear tests (a) and (b):  
 (a) & (b) Shear tests (Zakharov et al, 1970)  
 (c) Shear stress deformation (Suhara et al, 1974)  
 (d) Critical shear stress of adhesion (Suhara et al, 1974).

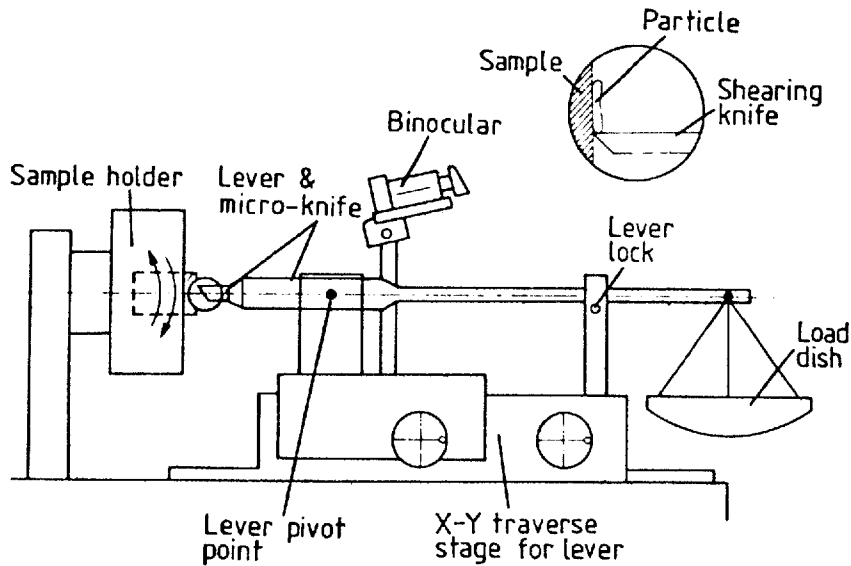


Figure 5.6: An instrument for measuring the adhesion strength of the particles (Rykalin and Kudinov, 1976).

The interaction time is expressed by:-

$$t = -\frac{1}{\nu} \ln \left( 1 - \frac{N(t)}{N_0} \right) \exp \left( \frac{E_a}{kT} \right) \quad \dots (5.4)$$

where  $\nu$  = oscillation frequency of atoms ( $\text{sec}^{-1}$ )

$E_a$  = activation energy ( $\text{J mole}^{-1}$ )

$k$  = Boltzmann's constant ( $1.38 \times 10^{-23} \text{ JK}^{-1} \text{ atom}^{-1}$ )

$T$  = contact temperature between particles and substrate (K)

Also:-

$$\frac{N(t)}{N_0} \sim \frac{\sigma(t)}{\sigma_m} \quad \dots (5.5)$$

where  $\sigma(t)$  = strength developed in time  $t$

$\sigma_m$  = maximum strength at the end of the process.

From the results presented by Rykalin and Kudinov (1976) and by manipulation of equations 5.3, 5.4 and 5.5 an estimate of the ratio of  $\sigma(t)/\sigma_m$  can be made and its variation with particle velocity and substrate temperature qualitatively analysed. Thus by combining

equations 5.3 and 5.4, equation 5.6 follows:

$$v = K \exp \left( \frac{E_a}{kT_k} \right) \quad \dots (5.6)$$

By assuming a reaction that is equivalent to the rate of solidification of the droplets on the substrate surface, the expression  $N(t)/N_0$  can be calculated by rearranging equation (5.4).

$$\frac{N(t)}{N_0} = \left| 1 - \exp \left( \frac{-tv}{\exp \left( \frac{E_a}{kT_k} \right)} \right) \right| \quad \dots (5.4b)$$

$$\approx \frac{\sigma(t)}{\sigma_m} \quad \dots (5.5)$$

The values calculated for a reaction time of  $10^2$  and  $10^3$  micro-seconds are shown in Table 5.1. The last column of Table 5.1 shows the periods of time at which the relative strengths of the particles on the substrate are equal to 0.9. Thus the extent of the particle interface reaction increases with both increasing particle pressure and temperature and this agrees with the experimental observation that coating adhesion is improved under these conditions.

Table 5.1: Calculation of the Relative Strengths of Silver Particles Sprayed onto Silver\*

| T<br>°C | P<br>MPa | V<br>ms <sup>-1</sup> | E <sub>a</sub><br>KJ mole <sup>-1</sup> | ln K | v(x10 <sup>9</sup> )<br>s <sup>-1</sup> | N(t)/N <sub>0</sub><br>t=10 <sup>2</sup> μs | N(t)/N <sub>0</sub><br>t=10 <sup>3</sup> μs | t if<br>N(t)/N <sub>0</sub> =0.9 |
|---------|----------|-----------------------|-----------------------------------------|------|-----------------------------------------|---------------------------------------------|---------------------------------------------|----------------------------------|
| 710     | 9.8      | 30.6                  | 142                                     | 5.19 | 6.70                                    | 0.0178                                      | 0.1643                                      | 0.0128                           |
| 710     | 24.5     | 48.3                  | 136                                     | 5.52 | 4.53                                    | 0.0247                                      | 0.2209                                      | 0.0092                           |
| 710     | 34.3     | 57.2                  | 131                                     | 5.78 | 3.34                                    | 0.0319                                      | 0.2766                                      | 0.0071                           |
| 720     | 9.8      | 30.6                  | 142                                     | 5.30 | 6.27                                    | 0.0198                                      | 0.1815                                      | 0.0115                           |
| 720     | 24.5     | 48.3                  | 136                                     | 5.60 | 4.15                                    | 0.0267                                      | 0.2370                                      | 0.0085                           |
| 720     | 34.3     | 57.2                  | 131                                     | 5.80 | 2.89                                    | 0.0325                                      | 0.2813                                      | 0.0070                           |
| 730     | 9.8      | 30.6                  | 142                                     | 5.42 | 5.95                                    | 0.0223                                      | 0.2022                                      | 0.0102                           |
| 730     | 24.5     | 48.3                  | 136                                     | 5.69 | 3.85                                    | 0.0292                                      | 0.2561                                      | 0.0078                           |
| 730     | 34.3     | 57.2                  | 131                                     | 5.88 | 2.67                                    | 0.0351                                      | 0.3008                                      | 0.0064                           |

\* The velocity is calculated from  $P = \rho V^2$  (Suhara et al., 1974) where  $\rho$  is the density of the sprayed material, V the particle velocity and P the pressure exerted by the particle onto the substrate.

## 5.5 EFFECT OF SUBSTRATE AND COATING VARIABLES

### 5.5.1 Deposit Thickness

Some results of coating strength in relation to coating thickness, Lyashenko et al., (1969) and Sharivker (1967), are shown in Figure 5.7.

The tensile tests described in section 5.4.2 were evaluated and it can be seen that there is an apparent increase in the measured value of the adhesion strength of an alumina coating when using a conical pin (curve 1) in comparison to a cylindrical pin (curve 2). There were three regions of interest. In the thickness range greater than 0.7 mm adhesive failure took place and the experimental points fitted a straight line with a negative slope. Within a coating thickness range of 0.45 to 0.70 mm a mixed adhesive-cohesive failure occurred, while for thicknesses between 0.3 to 0.5 mm the failure was reported as pure cohesive and these represent the strength of the coating layer. For coatings of less than 0.1 mm thickness, failures occurred at the circumference of a circle corresponding to the pin diameter and thus the shear strength of the sprayed layer can be estimated. The area over which the shear stress acts is calculated by the product of the pin diameter and the coating thickness. Thin coatings cannot be tested by attaching a metal plug to the deposit surface due to possible penetration of the adhesive to the substrate. The experimental accuracy of these measurements is limited by compressive or tensile stresses which are generated at the boundary between the solidified coating and the base metal by the differential thermal expansion of the pin and disc (as in Figure 5.3), and these may subsequently weaken the attachment of the deposit to the substrate.

Zakharov et al., (1970), on the other hand, found that the bond strength increased continuously with a decrease in coating thickness (Figure 5.8). The resulting curve was assumed to approach the stress axis asymptotically. The extrapolated intersection point with the stress axis quantitatively characterised the magnitude of 'pure' adhesive failure whereas the stress value at which the stress levelled off with increasing coating thickness characterised 'pure' cohesive failure. An empirical relationship (equation 5.7) of the

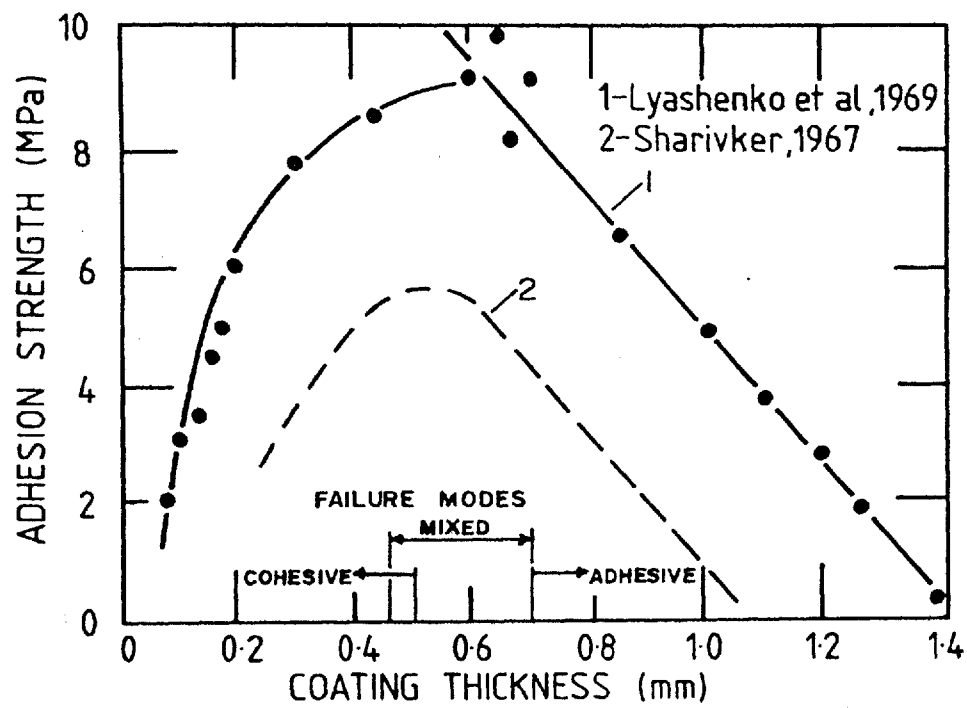


Figure 5.7: Adhesion strength data for alumina coated on a steel substrate. (1) Lyashenko et al., (1969)  
(2) Sharivker (1967).

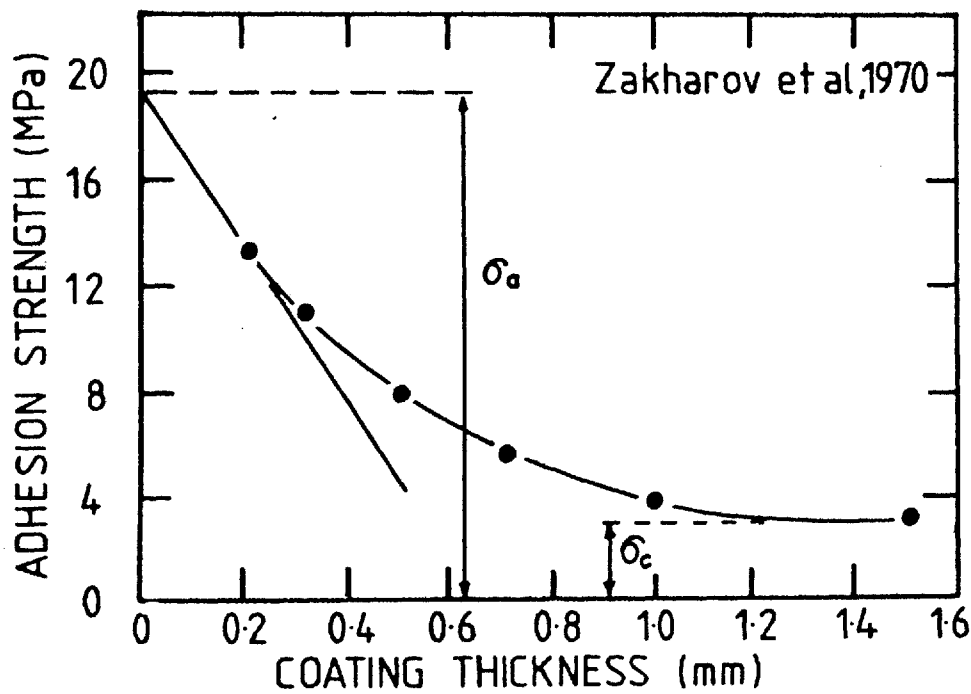


Figure 5.8: Adhesion strength data for zirconia coated onto a steel substrate (Zakharov et al., 1970).

relative bond strength and coating thickness was established for the case of stabilised zirconia deposited onto a steel substrate.

$$\frac{\sigma}{\sigma_a} = \frac{0.8}{3.2\delta} + 0.2 \quad \dots (5.7)$$

where  $\frac{\sigma}{\sigma_a}$  = the relative bond strength

$\sigma$  = measured bond strength of coating (Pa)

$\sigma_a$  = maximum bond strength of coating (Pa)

$\delta$  = coating thickness (mm)

It was claimed (Zakharov et al., 1970) that the bond strengths of deposits ranging from 0.2 to 1.5 mm in thickness could be established from bond strength measurements of a deposit 0.2 to 0.3 mm in thickness.

### 5.5.2 Profile of Grit Blasted Substrate

Although there are many views concerning the adhesion mechanism(s) of the coating to the substrate, there is general agreement that adhesion markedly depends upon the substrate surface preparation. For example Apps (1974a, 1974b) found that the type and condition of the grit blasting medium and the angle of blasting influenced the bond strength of flame sprayed aluminium coatings on steel, but that variations of blasting pressure, blasting speed and nozzle-substrate distance had no effect (Figure 5.9).

With chilled iron angular grit failure occurred mainly at the sprayed metal-substrate interface whereas with alumina grit the bond strength was increased and the location of failure moved to within the spray coating. The non-metallic grit led to a higher interfacial bond strength than chilled iron grit due to a more deeply cut surface and less surface debris. In both cases the level of bond strength was reduced when blunt grit or a low blasting angle was used. Even though grit blasting is the most common method of surface roughening, few studies have considered the effect of grit inclusions on the bond

strength. Other methods of substrate surface preparation include rough machining (Tucker, 1974) and chemical etching (Laszlo, 1961).

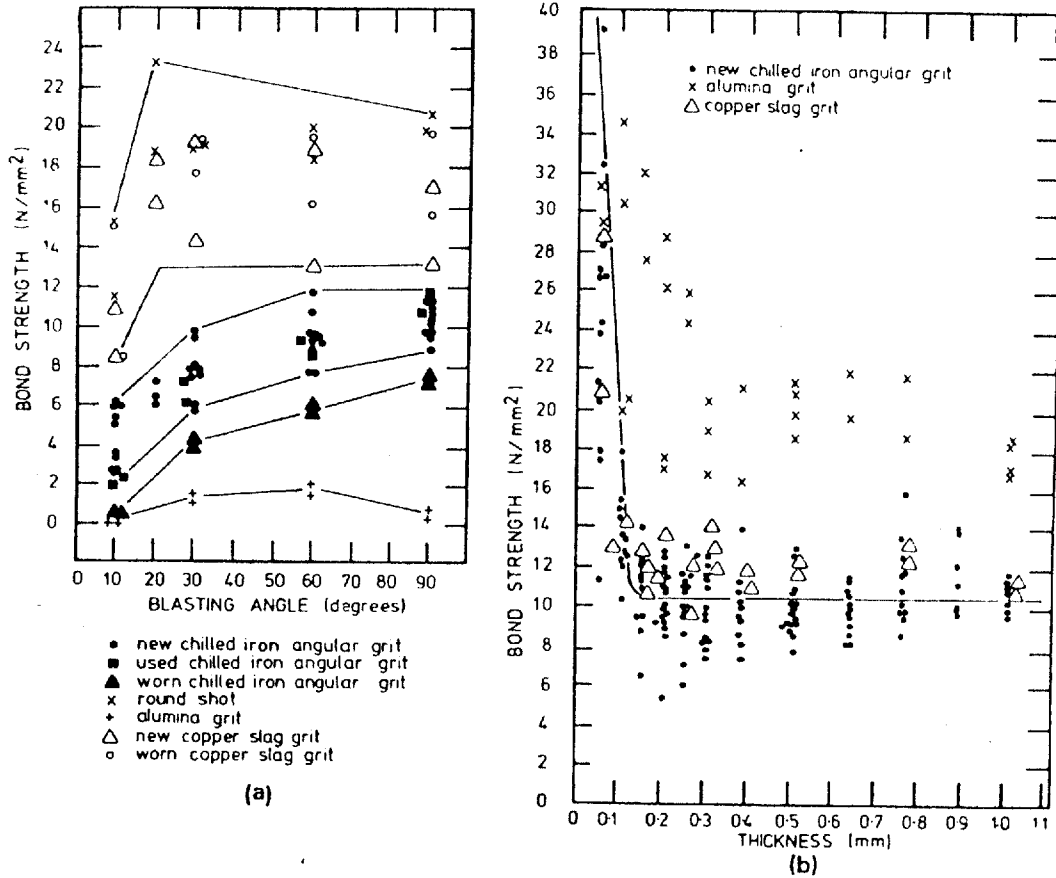


Figure 5.9: Variation of bond strength of aluminium coatings with (a) blasting angle; (b) coating thickness (Apps, 1974 a).

Bardal et al., (1973) characterised the surface profile by calculating the mean arithmetic deviation of the roughness (root mean square value or RMS):-

$$RMS = \sqrt{\frac{\sum (a_i^2)}{n}} \quad \dots (5.8)$$

where  $a_i$  = absolute value of the distance of the surface to the mean line;

where  $n$  = number of points taken into account.

Tests were carried out on mild steel blasted with common grit and sand and it was found that a variation of RMS values in the range

8 to 11  $\mu\text{m}$  did not have a significant effect on the adhesion of the coating (zinc or aluminium). At RMS values of less than 8  $\mu\text{m}$  the coating adhesion was found to be inferior. Another method of defining the surface roughness (Herpol and Tavernier, 1966) uses the centre line average (CLA) parameter:-

$$\text{CLA} = \frac{1}{n} \sum |a_i| \quad \dots (5.9)$$

where both  $n$  and  $a_i$  have been defined previously.

These numerical methods of presenting the surface profile have a major shortcoming in that they do not convey any information about the shape of the irregularities of the surface. Thus a coating having a great number of narrow zones in the form of sharp irregularities may very well have the same RMS (or CLA) value as a coating having a small number of broad zones. However the coating process will be affected by the surface area and profile and, even though the surface roughness measurements of two coatings may be the same, the spraying deposition and adherence may be significantly different. Thus the role of surface roughness and its influence on adhesion remains to be answered. The major contribution of surface roughness to coating adhesion may not only be the provision of sites for mechanical keying of the deposit, but could, in addition, either increase the surface energy due to a greater degree of plastic deformation (Epik et al., 1966) or possibly by exposing a greater area of clean, highly active surface (Tucker, 1974).

### 5.5.3 Interactions of Particles with Polished Substrates

Examination of the deposit structure of tungsten and zirconia sprayed onto glass and polished substrates of stainless steel, tungsten and copper (Grisaffe and Spitzig, 1963) indicated that the substrate thermal conductivity exerted the greatest control on the quench rate of the particles and greatly influenced the particle-to-substrate bond. The zirconia particles splashed considerably more than tungsten particles (Figure 5.10).

$v$  = Velocity (m/sec)  
 $T$  = Temperature ( $^{\circ}\text{C}$ )

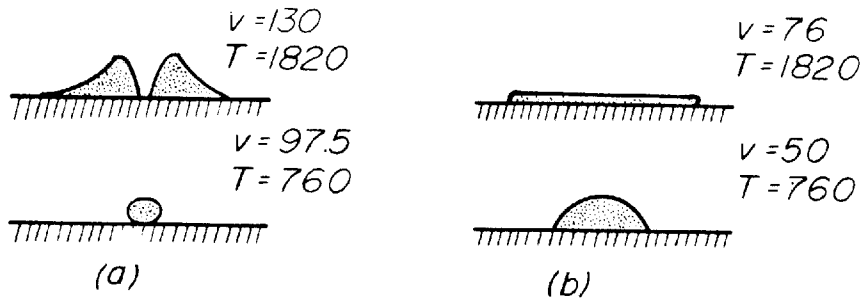


Figure 5.10: Particle impact profiles for (a) zirconia and (b) tungsten plasma sprayed particles (Grisaffe and Spitzig, 1963).

The adhesion of both materials, when sprayed in air, was very similar for any one substrate material. For example zirconia exhibited almost no adhesion to tungsten or copper and fragmented on impact against the substrate. On the other hand tungsten deformed on impact with no adhesion taking place. The adhesion of tungsten was greater than that exhibited by zirconia when sprayed onto stainless steel substrates and this was explained by the very much greater thermal expansion of zirconia, Table 5.2.

Table 5.2: Thermal Properties of Powders and Substrates (Grisaffe and Spitzig, 1963).

| Material            | Thermal Conductivity<br>near $20^{\circ}\text{C}$<br>$\text{J-cm/cm}^2\text{s}^{\circ}\text{C}$ | Specific Heat<br>near $20^{\circ}\text{C}$<br>$\text{J/g}^{\circ}\text{C}$ | Thermal Expansion<br>near $20^{\circ}\text{C}$<br>$\text{cm/cm}^{\circ}\text{C}$ |
|---------------------|-------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| <u>Powders</u>      |                                                                                                 |                                                                            |                                                                                  |
| Tungsten            | 1.662                                                                                           | 0.138                                                                      | $4.59 \times 10^{-6}$                                                            |
| Zirconia            | 0.021                                                                                           | 0.419                                                                      | $\sim 9.90 \times 10^{-6}$                                                       |
| <u>Substrates</u>   |                                                                                                 |                                                                            |                                                                                  |
| Glass               | 0.017                                                                                           | 0.754                                                                      | $8.14 \times 10^{-6}$                                                            |
| 304 Stainless steel | 0.163                                                                                           | 0.502                                                                      | $17.82 \times 10^{-6}$                                                           |
| Tungsten            | 1.662                                                                                           | 0.138                                                                      | $4.59 \times 10^{-6}$                                                            |
| Copper              | 3.939                                                                                           | 0.385                                                                      | $16.56 \times 10^{-6}$                                                           |

The relative thermal expansion coefficients of the substrate and deposit materials are not the only factors which affect the coating adhesion. Thus deposits which are coated onto substrates with similar expansion coefficients (for example stainless steel and copper) may have different adhesion strengths. Grisaffe and Spitzig (1963) suggest that this property can be related to the thermal conductivities of the materials; a substrate with a greater thermal conductivity tends to be associated with increased adhesion of the coating. A consequence of this property was that when plasma spraying was carried out at a higher substrate temperature, the adhesion of a tungsten deposit improved due to increased thermal conductivity of the substrate.

Hasui et al, (1970) carried out similar tests with plasma sprayed alumina on a polished mild steel substrate. On a cold substrate at ambient temperature the impacting particles formed a characteristic "stringer" or splash pattern, as described previously for a zirconia deposit. At a substrate temperature of  $380^{\circ}\text{C}$  the deposit changed to a flattened circular shape similar to that observed by Grisaffe and Spitzig (1963) for tungsten. Glass plates were also plasma sprayed and the stress pattern set up in the plate, as observed from the interference fringes, was used as a measure of deposit adhesion. When deposition was carried out onto a heated glass plate no interference fringes were observed and this was related to an increased adhesion of the coating.

Rykalin and Kudinov (1976) examined the fracture surfaces of silver particles which were sheared from a polished silver substrate (section 5.4.4). In the initial stages of the deposition process only single particles were firmly joined to the base material. As the number of such particles increased the adhesive strength of the deposit increased until at the maximum strength the spots of particles sticking to the substrate filled the entire contact surface. It was calculated that, for the majority of materials, the particle solidification time amounted to about 1-100 microseconds. In addition the thermally affected zone under the particle did not exceed a depth of 20-30  $\mu\text{m}$  and the temperature gradients reached  $10^5 \text{ K cm}^{-1}$ .

Scanning electron micrographs of the fracture surfaces at

the particle-substrate interface showed a dimpled character which appeared to be characteristic of failure through a diffusion bonded zone. If the coating was mechanically bonded then some detail of the original surface profile would be expected to remain after failure at the interface. It must be remembered however that this work involved the use of large droplets of silver (about 0.3 mm in diameter) and the thermal history of these at the interface would be quite different to that of sprayed coatings.

#### 5.5.4 Residual Stresses in Coatings

When the coating particles are cooled very rapidly from their melting points or above to about 50–150°C both transient and residual stresses are created. The transient stress occurring in a localised region results from the difference in the mechanical response of the substrate and the coating layers previously deposited, to the rate at which heat can be removed from the area. These stresses can be high but are unimportant unless they cause immediate cracking of the coating. The amount of residual stress in a coating is dependent on the temperature gradient generated in the coating and substrate during spraying. If the coating surface is not kept at room temperature during the spraying operation, there will be a change in the stress distribution on cooling to ambient temperature due to the difference in the coefficients of thermal expansion between the coating and substrate. The value of the residual stress increases in a linear manner with respect to the coating thickness, if both the substrate composition and thickness, and the deposit composition and surface preparation are kept constant. Tucker (1974) describes an experiment to demonstrate this where nickel coatings were deposited onto aluminium cylinders. Split rings and slots were used to measure both the circumferential and longitudinal stresses.

During the spraying of a refractory coating onto a metal the thermal distribution illustrated in Figure 5.11a is established (Marynowski et al., 1965).

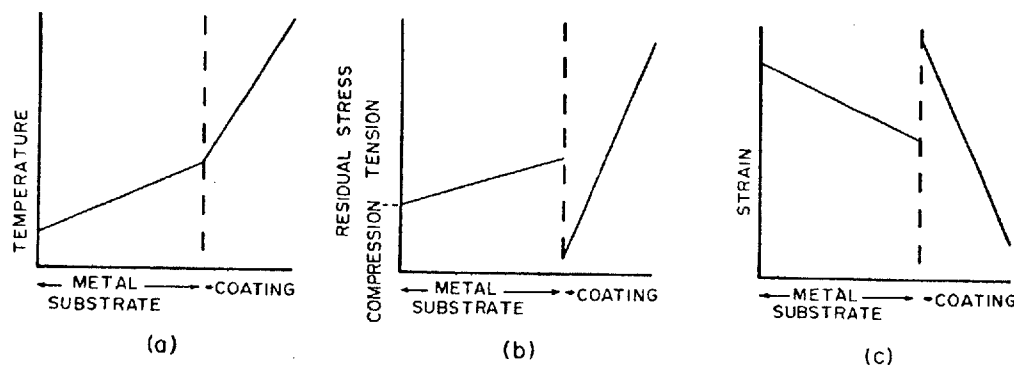


Figure 5.11: Spray deposition of a refractory onto a metal:  
 (a) thermal distribution;  
 (b) stress distribution;  
 (c) strain distribution.  
 (Marynowski et al., 1965).

The small temperature rise that occurs in the metal, and the larger thermal gradient in the coating reflects the different thermal conductivities of the metal and substrate. On cooling to room temperature the metal at the interface will attempt to shrink more than the deposit material; and the coating surface, which was hottest during spraying, has the greatest shrinkage.

The relationships of the residual stress and strain to the coating thickness are schematically represented by Figure 5.11(b) and (c). It is evident that high stresses at the interfacial area will tend to produce an adhesive failure, and the high tensile stress at the coating surface may result in surface cracking of the coating. Marynowski et al., (1965) calculated the residual stresses at the interface and surface while coating 6.4 mm thick copper and iron substrates with a 2.5 mm thick coating of TiC (Table 5.3).

Methods of reducing the thermal gradients imposed upon a structure includes either gas-cooling the front surface during spraying or by heating the substrate uniformly to some elevated temperature. Preheating the substrate may reduce the surface tensile stress but considerably increases the interfacial stresses. The presence of residual stresses has a significant effect on the bond strength of a coating and these must be considered in conjunction with mechanical strain during the service life of the coating. Thus, since the outer portion of the coating is usually in tension the fracture stress will be slightly less than the calculated properties of unloaded specimens.

Table 5.3: Stresses Introduced During Plasma Spraying a 2.5 mm Coating of TiC on a Metal Substrate (Marynowski et al., 1965).

| Spray Conditions                                                                                          | Temperature<br>at back of<br>Substrate<br>°C | Compressive<br>Stress at<br>Interface<br>(MPa) | Tensile Stress<br>at Coating<br>Surface<br>(MPa) |
|-----------------------------------------------------------------------------------------------------------|----------------------------------------------|------------------------------------------------|--------------------------------------------------|
| <u>Fe Substrate</u>                                                                                       |                                              |                                                |                                                  |
| (1) Stationary position                                                                                   | 38                                           | 132                                            | 197                                              |
| (2) Traverse at 50 mm sec <sup>-1</sup>                                                                   | 38                                           | 6                                              | 231                                              |
| (3) 1 sec pause in traverse                                                                               | 38                                           | 24                                             | 267                                              |
| (4) Traverse at 50 mm sec <sup>-1</sup> }<br>Front surface cooling                                        | 38                                           | 5                                              | 95                                               |
| (5) Traverse at 50 mm sec <sup>-1</sup> }<br>Front surface cooling<br>(heated to elevated<br>temperature) | 93                                           | 25                                             | 55                                               |
| <u>Cu Substrate</u>                                                                                       |                                              |                                                |                                                  |
| (6) Stationary position                                                                                   | 38                                           | 55                                             | 344                                              |
| (7) Stationary position }<br>(heated to 538°C)                                                            | 538                                          | 569                                            | 687<br>(Compressive)                             |

Hasui and Kitahara (1966) found the residual stresses in Mo, Ni-base alloy and alumina coatings that were flame and plasma sprayed onto a grit-blasted mild steel substrate. The residual stresses were estimated by spraying one face of mild steel specimens (1.5 x 10 x 130 mm) and measuring the amount of deflection of the bar. The average residual stress ( $\sigma_r$ ) was calculated by applying the formula

$$\sigma_r = \left\{ \frac{(h_1^3 E_1 + h_2^3 E_2)}{6\rho h_1(h_1+h_2)} + \frac{E_1(h_1^3 E_1 + h_2^3 E_2)}{12\rho^2(h_1 E_1 + h_2 E_2)} + \frac{E_1 E_2 h_2(h_1 + h_2)}{2\rho(h_1 E_1 + h_2 E_2)} \right\} \frac{1}{(1-\mu^2)}$$

... (5.10)

where  $E_1, E_2$  = Young's Modulus of the coating and substrate respectively;

$h_1, h_2$  = thicknesses of the coating and strip respectively

$\rho$  = radius of curvature of the deflected strip (measured on a 80 mm length).

$\mu$  = Poisson's ratio (approximately 0.3).

The strips, after being grit blasted were annealed at  $850^{\circ}\text{C}$  for 30 minutes, presumably so that an initial stress free state could be achieved. Molybdenum coatings with a thickness of 0.35 to 0.40 mm were found to have a residual tensile stress whereas coatings thicker than 0.40 mm had a residual compressive stress (Figure 5.12a). For nickel alloy coatings (Figure 5.12b) tensile residual stresses were observed irrespective of thickness and the value of this stress increased with thicker coatings. On the other hand, residual stresses for alumina were compressive (Figure 5.12b). Generally the stresses resultant from the flame spraying process were greater than those from the plasma spraying operation. No reasons were proposed for the variable stress patterns produced by spraying different deposit materials but the results are in good agreement with the work of Marynowski et al., (1965). Thus as the thermal conductivity of the deposit material increases the residual stresses at the surface change from compressive (i.e. alumina) to tensile (i.e. nickel alloy and molybdenum).

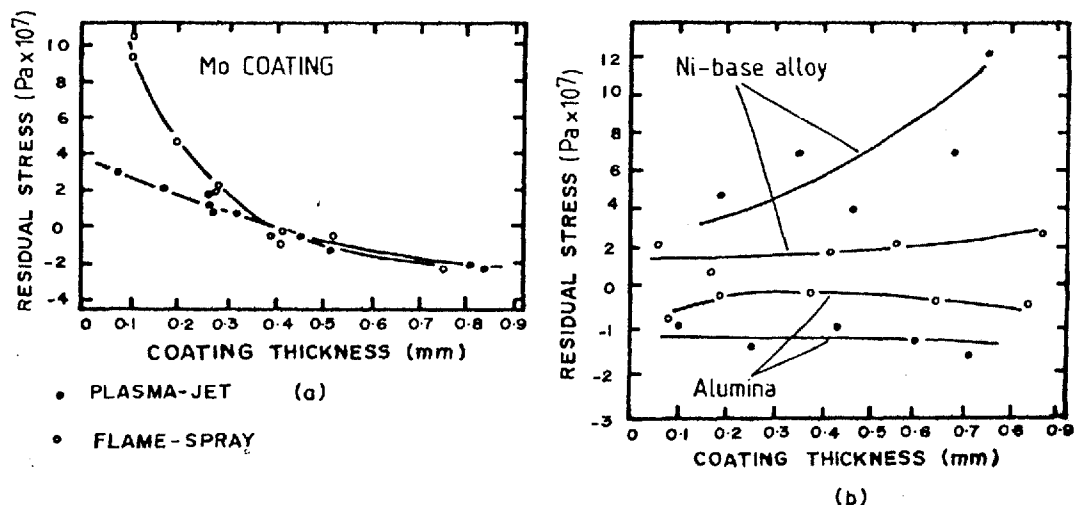


Figure 5.12: Relation between residual stress and coating thickness for flame and plasma sprayed coatings (Hasui and Kitahara, 1966).

- (a) Molybdenum coatings
- (b) Ni-base alloy and alumina coatings.

## 5.6 METALLOGRAPHIC TECHNIQUES AND EXAMINATIONS

### 5.6.1 Optical Metallography

Many investigators have used standard metallographic techniques where the coating and substrate are embedded in a cold setting resin. Matting and Steffens (1967) did not consider that these techniques gave a reliable analysis of the grit blasted surface since the mechanical polishing operation always disturbed the fine structure of the substrate material. They determined, from a specially designed specimen, that the surface of a grit-blasted substrate consisted of severely torn, high-energy regions.

The fracturing process for both arc and flame sprayed coatings onto steel was examined with the aid of a microscope (Matting and Steffens, 1967). The fracture path in flame sprayed coatings followed the substrate-coating interface, whereas arc sprayed coatings tended to fracture inside the coating. In the latter case fracture originated mainly from smooth thin oxide films and occurred if the deposit particles had regular, smooth surfaces. The cracks often ran parallel to the particle boundaries, and crystalline transition regions were observed between the substrate and the deposit. Thus it was suggested that local melting of the substrate had taken place at the interface, and that these areas key the coating to the substrate so that the adhesive strength of the coating is greater than its cohesive strength.

### 5.6.2 Chemical Composition of the Substrate-Coating Interface

Studies aimed at finding the chemical composition of the constituents at the deposit-substrate interface have been made to resolve the mechanism of coating adhesion. Many workers (Kitahara and Hasui, 1974; Suhara et al., 1974; Steffens, 1966; Matting and Steffens, 1967) have carried out X-ray microprobe element scans across the interface and found a decrease of the deposit constituents towards the substrate material. Kitahara and Hasui (1974) also

performed tests on spray coatings and related the failure mechanism to the microprobe analysis results. Failure at the interface occurred when there was a sharp concentration drop of the deposit material at the interface; which also corresponded to an abrupt concentration difference of the substrate material. Cohesive failure occurred when the relative concentration change of the deposit and substrate materials was gradual.

Kitahara and Hasui (1974) used Cu and Co K $\alpha$  radiation to analyse the composition of the "adhesive layer" formed at the boundary between the coating and substrate. The thickness of the substrate must be less than the depth of the X-ray penetration for analysis of the interface material from the substrate side, and thus aluminium and iron foils of 35  $\mu$  and 15  $\mu$  thickness respectively were used as the substrate. The foil substrates were then placed onto a ceramic plate and Ni, Cr, Mo, Ta and W coatings of 0.1 to 0.2 mm thickness deposited. The composition of the interface material was determined, Table 5.4, and in most cases an intermetallic compound was observed which suggested that the substrate material had been melted and then reacted with the impinging particles. Whether the same reactions would take place in the more practical case in which the substrate was thicker is not clear from the results presented by Kitahara and Hasui. If the substrate thickness was increased, the rate of heat removal from the interface region would also be increased

Table 5.4: Composition of Boundary Layers Between Coating and Substrate (Kitahara and Hasui, 1974).

| Substrate  | Ni                       | Cr                     | Mo                                               | Ta                       | W                                                  |
|------------|--------------------------|------------------------|--------------------------------------------------|--------------------------|----------------------------------------------------|
| Al         | $\text{Al}_3\text{Ni}^a$ | $\text{Al}_5\text{Cr}$ | $\text{Al}_3\text{Mo}$                           | $\text{Al}_2\text{Ta}$   | $\text{WAl}_{12}$                                  |
| Mild Steel | ...                      | ...                    | $\sigma\text{-FeMo}^a$<br>$\text{Fe}_2\text{Mo}$ | $\text{Fe}_7\text{Ta}_3$ | $\text{Fe}_2\text{W}$<br>$\text{Fe}_7\text{W}_6^a$ |

<sup>a</sup>Temperature of formation :  $\text{Al}_3\text{Ni}$ : 842°C, 854°C

$\sigma\text{-FeMo}$ : 1540°C

$\text{Fe}_7\text{W}_6$ : 1640°C

and the formation of intermetallics suppressed. Another method of examining the constituents at the interface of a thick specimen, without the generation of any heating effects due to the low thermal conductivity of a ceramic backed foil substrate, would be to progressively thin the thick substrate material by either a machining or a chemical etching operation. After progressive removal of the substrate material the new surface could be examined by the above X-ray technique.

### 5.6.3 Electron Microscopy

Recently electron microscopical techniques have been used to determine the structural and morphological aspects of coating deposition in relation to their physical properties. Koubek (1970) flame and plasma sprayed alumina of 50 to 100  $\mu\text{m}$  in diameter onto a grit blasted aluminium substrate and found that the maximum density of the deposit depended on a balance between the heat input and particle velocity. At low flow rates of the ionising gas (nitrogen) the residence time of the powder in the flame increased but the impact velocity decreased. However at high flow rates the particles were not sufficiently heated even though the impact velocity was increased. A high density deposit consisted of an orderly arrangement of flattened solidified droplets in a lamellar structure. Low density deposits resulted from either incomplete melting of the particles, or at the other extreme, vaporisation of over-heated droplets. Porosity within individual droplets was thought to be nitrogen gas which evolved from metal nitrides which were formed in the plasma flame but decomposed on contact with air. Such an explanation offers a reason why shielding of the plasma flame and substrate with an inert gas decreases the porosity of the deposit; but does not clarify why argon does not reduce the amount of porosity within particles when it is used as the ionising gas.

Other investigators (Wilms and Herman, 1976) examined the mechanism by which yttria additions decreased the porosity of alumina coatings on steel from 15% to 7.5%. Scanning and transmission electron microscopy were used to characterise morphological and microstructural details of the deposits; and mercury

intrusion porosimetry and small angle neutron scattering were used to find the porosity. The technique of small angle neutron scattering has a major advantage over mercury intrusion porosimetry in that the amount of internal closed porosity can be determined. An amorphous or glassy matrix was formed in high yttria (10 - 20% wt) deposits and it was suggested that this became rigid at temperatures below the solidification temperature of the crystalline alumina. The amorphous phase flowed more readily to :

- (i) interact with the sand blasted substrate surface and
- (ii) fill the interstices between the platelets of the crystalline alumina.

The addition of the yttria also increased the adhesion strength of the coating (Figure 5.13).

It was proposed (Wilms and Herman, 1976) that the yttria increased the degree of chemical interaction taking place at the substrate-coating surface. There appeared to be a significant incorporation of the iron into the alumina with little diffusion of aluminium into the substrate. Iron oxides were thought to be formed on the substrate surface during the plasma coating operation and these subsequently reacted with the molten alumina to form an aluminium-

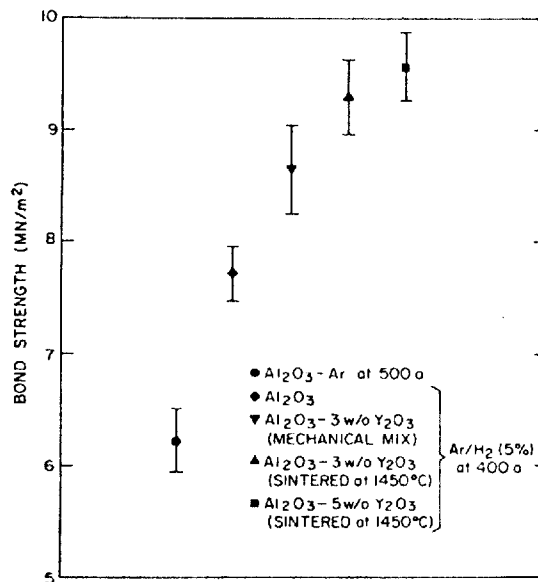


Figure 5.13: Tensile adhesion strengths of Al<sub>2</sub>O<sub>3</sub> base deposits sprayed onto steel (Wilms and Herman, 1976).

iron spinel. The substrate-coating interface thus formed a chemical bond which was supplemented by a mechanical bond dependent upon the substrate surface preparation and the presence of any second phase material.

Safai and Herman (1977) have reported scanning and transmission electron microscopic studies of plasma and flame sprayed aluminium coatings on mild steel substrates. The grains in the first region of a particle to solidify were orientated with the longitudinal axis perpendicular to the substrate surface. As the particle flattened the direction of its mass movement changed from normal to lateral with respect to the substrate surface; and the heat transfer path changed to a direction either towards the particle core or to its edges. Therefore it was observed that the grains on the rim of a quenched particle were elongated with their longitudinal axis parallel to the substrate surface (Figure 5.14). Particles located away from the substrate did not show these characteristics because they experienced a low quenching rate. They were composed of large equiaxed grains which were randomly orientated to a degree largely determined by the topology of the substrate surface. The asperities of a grit blasted substrate surface restricted any flow of the impinging particles and the substrate profile eliminated any apparent grain morphology.

Two types of porosity were observed (Safai and Herman, 1977). Most of the porosity was associated with pores located between the deposited layers and elongated in the plane of the substrate but other pores were approximately spherical and resulted from dissolved gases in the deposit material. Any oxides which formed on the particle

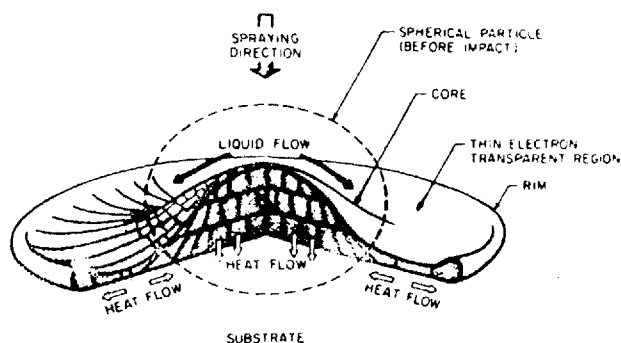


Figure 5.14: Heat flow in a plasma sprayed particle (Safai and Herman, 1977).

during coating usually shattered on impact and decreased both the flowability of the molten droplet and the extent of any inter-particle reaction. Thus the cohesive strength of the coating can be decreased by high porosity or the presence of oxide films. Porosity decreases the load bearing area of the coating while any oxide films may provide a path for crack propagation.

## 5.7 CONCLUSIONS

The literature on flame and plasma sprayed coatings although abundant, does not clarify the mechanism controlling adhesion of the coating to the substrate. Many investigators have proposed that impacting particles are in a fluid state and flow around protuberances of the substrate to form a mechanical key. The effects of the substrate surface preparation on the adhesive strength of the coating and the results of X-ray analysis have been presented to show that no chemical reaction occurs. On the other hand X-ray and microscopic examination has revealed microcrystallite growth at the coating-substrate interface, and evidence of a concentration gradient of the coating material into the substrate has been obtained by microprobe analysis. The latter observations suggest that some reaction does occur at the interface. Differences in adhesive strength from one coating material to another also suggest that adhesion is not controlled only by a mechanical keying effect.

The extremely high rates at which sprayed particles solidify on impact with the substrate means that chemical reaction at the interface must be very limited. In general chemical reaction is not a pre-requisite for good bonding of coatings and it is probable that the bond strength of plasma sprayed coatings is controlled primarily by physical mechanisms.

Another important factor influencing coating adhesion is the residual stress system developed as the coating solidifies and cools. Residual stresses have been estimated theoretically and also directly measured. These studies have been concerned mainly with the influence of the physical properties of the coating and substrate materials (thermal conductivity, thermal expansion coefficient and

specific heat) on interfacial and surface residual stresses, and their effect on coating adhesion.

A wide range of techniques for determining the coating adhesion have been reported. The data obtained are generally not suitable for use in design. They are commonly used for comparison between different coatings and application conditions or for acceptance tests. Results have commonly been reported as "cohesive" or "adhesive" failure; however the fracture appearance and failure mechanism have rarely been studied in detail. This is an area of research which should be investigated thoroughly because any realistic discussion of the mechanism of adhesion must be based on a knowledge of the mechanism by which the coating fails. Scanning electron microscopy combined with analytical facilities provides a powerful tool for the investigation of the nature of coating failure.

Optical and scanning electron microscopy have been used to study the structure of sprayed coatings and the formation and distribution of porosity. All of these studies have been concerned with the effects of spraying parameters on microstructure. The structure of coatings has not been studied in terms of the parameters directly controlling coating formation; namely the size, velocity and temperature of the impacting particles. This is undoubtedly due to the difficulty in direct measurement of these parameters and the fact that many of the diagnostic techniques used disturb the spraying conditions. Theoretical studies of heat and mass transfer characteristics of the plasma and flame spraying processes have not significantly contributed to an understanding of the factors controlling coating quality.

It is apparent from the literature that there has been very little work carried out on the central problem of adhesion of plasma and flame sprayed coatings, namely direct determination of the mechanism by which the coating is detached from the substrate and the manner in which this is influenced by the nature of the substrate surface, residual stresses in the coating, coating microstructure and interaction between the sprayed particles and substrate.

## CHAPTER SIX

### THE APPLICATION OF FRACTURE MECHANICS TO THE MEASUREMENT OF COATING ADHESION

#### 6.1 NOMENCLATURE

|        |   |                                             |
|--------|---|---------------------------------------------|
| A      | - | crack area                                  |
| $A_1$  | - | area enclosed under loading trace (J)       |
| b      | - | specimen arm width (or crack width) (m)     |
| C      | - | compliance ( $\text{m N}^{-1}$ )            |
| DCB    | - | double cantilever beam                      |
| DT     | - | double torsion                              |
| DV     | - | digital voltage                             |
| E      | - | Young's modulus (Pa)                        |
| F      | - | Force (N)                                   |
| G      | - | strain energy release rate                  |
|        | - | crack opening force                         |
|        | - | fracture toughness ( $\text{J m}^{-2}$ )    |
| gsf    | - | geometric stability factor                  |
| h      | - | specimen arm thickness (or beam height) (m) |
| K      | - | stress intensity factor                     |
|        | - | fracture toughness ( $\text{N m}^{-3/2}$ )  |
| $\ell$ | - | crack length (m)                            |
| M      | - | bending moment (N-m)                        |
| N      | - | load setting of tensometer                  |
| $R_1$  | - | range setting of extensometer               |
| $R^2$  | - | coefficient of determination                |
| S      | - | shear modulus (Pa)                          |
| t      | - | total specimen thickness (m)                |
| $t_n$  | - | thickness at notched region of specimen (m) |
| U      | - | total energy (J)                            |
| $U_E$  | - | elastic potential energy (J)                |

|                 |   |                                                                  |
|-----------------|---|------------------------------------------------------------------|
| $U_S$           | - | free surface energy (J)                                          |
| $W$             | - | total specimen width (m)                                         |
| $W_L$           | - | work undergone by outer boundary of a body (J)                   |
| $\frac{W_m}{2}$ | - | bending moment arm for DT specimen (m)                           |
| $\alpha$        | - | empirical constant which implies bending beyond the crack tip    |
| $\beta$         | - | empirical constant to account for displacements at the crack tip |
| $\gamma$        | - | energy of one surface of a crack ( $J\ m^{-2}$ )                 |
| $\Delta$        | - | displacement (m)                                                 |
| $\mu$           | - | displacement<br>elastic elongation (m)                           |
| $\nu$           | - | Poisson ratio.                                                   |

### Subscripts

|          |   |                                           |
|----------|---|-------------------------------------------|
| I,II,III | - | cracking modes                            |
| C        | - | critical value at onset of cracking       |
| E        | - | extensometer measurement                  |
| F        | - | final measurement                         |
| G        | - | grip measurement                          |
| I        | - | initial measurement                       |
| LP       | - | measurement taken at the loading point    |
| TLP      | - | true value between the loading points     |
| TOT      | - | total value                               |
| S        | - | Measurement of parameter for the specimen |

## 6.2 INTRODUCTION

It has been shown in Chapter 5 that although the tensile adhesion test is quite useful in determining the bond strength of a coating and can be used to establish the relative merits of different coatings, it has a number of disadvantages as a means of studying the mechanism of adhesion. The major disadvantages of the tensile adhesion test are summarised below.

- (1) A high strength adhesive is needed to join the loading fixture to the coating and the effect of this on the coating properties is unknown.
- (2) It is not known how the tensile adhesion strength relates to the stresses imposed on the coating during its service life.
- (3) The tensile adhesion test does not allow a quantitative analysis of factors controlling the failure mechanism of coatings, and a study of this nature will lead to improvements in plasma spray technology.

Another approach, which has been successfully used for studying the adhesion of organic coatings, makes use of fracture mechanics and measures a parameter associated with the propagation of a crack in the vicinity of the interface. Thus the adhesive joins two metal bars together (usually aluminium) and crack growth at the interface between these components is used to measure the energy expended in creating new fracture surfaces.

Two parameters which relate to the cracking process can be defined.

- (1) The stress intensity factor ("K" in units of  $\text{Pa m}^{1/2}$  or  $\text{N m}^{-3/2}$ ) is a measure of the stress distribution at the crack tip and is primarily a function of the crack tip radius, specimen geometry and the material properties. This factor should not be confused with the stress concentration factor which is the ratio of stress intensification relative to the applied stress that arises due to the presence of notches.

- (2) The strain energy release rate parameter (or crack extension force "G" in terms of  $\text{J m}^{-2}$  or  $\text{N m}^{-1}$ ) measures the energy needed to either initiate cracking or to propagate a crack and is thus particularly appropriate under conditions where the crack front geometry is not well defined.

Both of these terms are also referred to as the "fracture toughness". These parameters are defined for any stress state of the specimen but the particular value at the onset of cracking is called the critical value and indicated by a subscript "C". The material properties of G and K are related in a manner which is shown in section 6.3.

The specimen geometry and loading arrangement can be chosen such that failure occurs either:-

- (i) under the action of tensile stresses,
- (ii) by shearing in a direction normal to the crack front, or
- (iii) by shearing in a direction parallel to the crack front (Figure 6.1) and these are referred to as mode I, mode II and mode III respectively. (Lawn and Wilshaw, 1975, pp. 51,52).

The failure mode of a test is also indicated by a subscript. The mode I test is the most pertinent to crack propagation in brittle solids since these cracks tend to orientate so that the shear loading is a minimum. Also the mode I type of test directly relates to the tensile adhesion test so these were chosen to study the adhesion of plasma sprayed coatings.

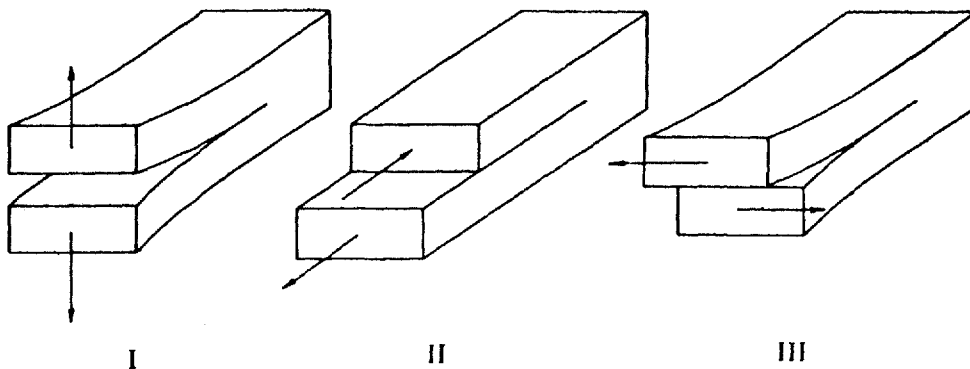


Figure 6.1: Modes of fracture.  
 I - opening  
 II - shearing normal to crack front  
 III- shearing parallel to crack front.

The fracture mechanics approach offers the possibility of determining a material parameter which is closely related to the difficulty of removing a coating, that is, it provides a useful measurement of "practical adhesion". The determination of such a parameter, which more directly reflects the true adhesion, then allows a quantitative approach to factors controlling adhesion; such as the surface finish of the substrate, preheating of the substrate and spraying variables (mainly torch to substrate distance and coating thickness). In this chapter experiments are detailed in which the principles of fracture mechanics are applied to testing the adhesion of plasma sprayed coatings.

### 6.3 PRINCIPLES OF FRACTURE TOUGHNESS TESTING

Griffith in 1921 (Hayes, 1975; Lawn and Wilshaw, 1975, pp. 1-15) originally formulated the energy balance criterion for a free crack in a solid body:-

$$U = (-W_L + U_E) + U_S \quad \dots (6.1)$$

where  $U$  = total energy (J or N-m)

$W_L$  = amount of work work undergone by the outer boundary of the body (J)

$U_E$  = strain potential energy which is stored in the elastic medium (J)

$U_S$  = free surface energy created by new crack surfaces (J).

The terms  $(-W_L + U_E)$  are grouped together and represent the mechanical energy contribution to the crack. As a crack grows the mechanical energy decreases and the surface energy increases. The Griffith equilibrium requirement is met when :-

$$\frac{dU}{d\ell} = 0 \quad \dots (6.2)$$

where " $\ell$ " is the crack length, at which condition a crack is stable. If this term is negative the crack will extend and if it is positive the crack will (according to theoretical considerations) close up.

The elastic strain energy can be calculated (Lawn and Wilshaw, 1975, pp. 49-51) if it is assumed that the opening and closing of the crack obeys Hooke's Law, as below:

$$\mu = CF \quad \dots (6.3)$$

where  $\mu$  = the elastic elongation of the test piece (m)  
 $C$  = the elastic compliance ( $m N^{-1}$ )  
 $F$  = the tensile force (N).

The strain energy is :-

$$\begin{aligned} U_E &= \left. \int_0^{\mu} F(\mu) d\mu \right\} \quad \dots (6.4) \\ &= \frac{1}{2} F\mu = \frac{1}{2} F^2 C \end{aligned}$$

and for incremental crack growth,

$$\delta\mu = C\delta F + F\delta C \quad \dots (6.5)$$

The mechanical energy term can now be calculated for two extreme conditions. Under constant force (or "dead weight") loading equation (6.5) reduces to  $F\delta C$  so that :-

$$\delta W_L \approx F\delta\mu = F^2\delta C \quad \dots (6.6a)$$

$$\delta U_E \approx \frac{1}{2} F^2\delta C \quad \dots (6.6b)$$

and the total mechanical energy is :-

$$\delta(-W_L + U_E) \approx -\frac{1}{2} F^2\delta C \quad \dots (6.7)$$

Under constant displacement (or "fixed grip") loading  $\delta\mu = 0$ , therefore:

$$\delta W_L = 0 \quad \dots (6.8a)$$

$$\delta U_E = -\frac{1}{2} F^2\delta C \quad \dots (6.8b)$$

and the total mechanical energy is :-

$$\delta(-W_L + U_E) = -\frac{1}{2} F^2 \delta C \quad \dots (6.9)$$

It can be seen that the mechanical energy released during incremental crack extension is independent of the loading configuration. An important distinction is that for constant displacement conditions the strain energy decreases (equation 6.8b) whereas under constant force the strain energy increases (equation 6.6b).

The strain energy release rate per unit width of crack front can now be defined for both constant loading and constant displacement conditions as:-

$$G = -\left(\frac{\partial U_E}{\partial \ell}\right)_{\mu \text{ or } F} \quad \dots (6.10)$$

or

$$G = \frac{1}{2} F^2 \frac{dC}{d\ell} \quad (F = \text{constant}) \quad \left. \vphantom{\frac{dC}{d\ell}} \right\} \quad \dots (6.11a)$$

$$G = \frac{1}{2} \left(\frac{\mu^2}{C^2}\right) \frac{dC}{d\ell} \quad (\mu = \text{constant}) \quad \left. \vphantom{\frac{dC}{d\ell}} \right\} \quad \dots (6.11b)$$

Since the compliance increases with crack length the above equations indicate that the value of  $G$  decreases during a constant displacement experiment in relation to a constant load test; and thus fixed grip loading always produces a more stable crack.

The area produced during crack advancement is associated with a surface energy of  $2\gamma$  (units of  $\text{J m}^{-2}$ ) which is in turn related to the strain energy release rate by the expression :-

$$G = 2\gamma \quad \dots (6.12)$$

It has been shown (Griffiths, 1978; Wachtman, 1974) that for plane strain conditions :-

$$G_I = \frac{(1 - \nu^2) K_I^2}{E} \quad \dots (6.13)$$

where  $G_I$  = strain energy release rate for a specimen under tensile loading ( $J\ m^{-2}$ )

$\nu$  = Poisson ratio

$K_I$  = stress intensity factor ( $N\ m^{-3/2}$ )

$E$  = Young's modulus ( $N\ m^{-2}$ )

The term  $K_I$  is related to the stress field near the crack tip (Wiederhorn, 1968) where the subscript I represents a loading mode such that displacements are perpendicular to the fracture plane. On combining equations (6.12) and (6.13) the fracture criterion (under plane strain conditions) becomes:-

$$K_I = \left( \frac{2\gamma E}{(1-\nu^2)} \right)^{1/2} \quad \dots (6.14)$$

The stress intensity factor and strain energy release rate are directly related through equation (6.13) but it must be kept in mind that the material property of Young's modulus may, for some visco-elastic materials, be highly dependent on the strain rate. The equations (6.11a) and (6.11b) show that the strain energy release rate is a continuous function of the crack length yet in practice (Gurney and Mai, 1972; Glucklich, 1971; Gurney and Ngan, 1971) the crack only grows when

$$\frac{dU}{d\ell} < 0 \quad \dots (6.15a)$$

Thus when a crack propagates it will proceed beyond the equilibrium position given by equation (6.11) and therefore,

$$\frac{dU}{d\ell} > 0 \quad \dots (6.15b)$$

There are a number of experimental techniques available to determine the fracture toughness parameters of  $K_{IC}$  and  $G_{IC}$  where the subscript "C" refers to the critical value which occurs at the onset of cracking. The distinction between the various methods essentially lies in the geometry of the specimens and the manner of load application (Evans, 1974). Only those techniques which are directly relevant to this thesis will be examined.

## 6.4.1 Literature Survey

The double torsion test (DT) requires a four point bending load to be applied to one end of a rectangular beam (Figure 6.2); (Outwater and Gerry, 1969; Kies and Clark, 1969). The test is ideally suited for opaque materials (Evans, 1972; McKinney and Smith, 1973), where crack length is not easily measured, because cracking occurs at a constant strain energy release rate or stress intensity factor (equations 6.16 and 6.17).

$$G_{IC} = \frac{3F_C^2 W_m^2}{8t^3 t_n W S} \quad \dots (6.16)$$

where  $F_C$  = critical force (N)

$W_m/2$  = bending moment arm (distance between the inside and outside loading points) (m)

$t$  = total specimen thickness (m)

$t_n$  = specimen thickness in notched region (m)

$W$  = total specimen width (m)

$S$  = shear modulus of material ( $N m^{-2}$ ).

and,

$$K_{IC} = \frac{F_C W_m}{2} \left[ \frac{3(1 + \nu)}{W t^3 t_n} \right]^{1/2} \quad \dots (6.17)$$

where additionally  $\nu$  = Poisson's Ratio.

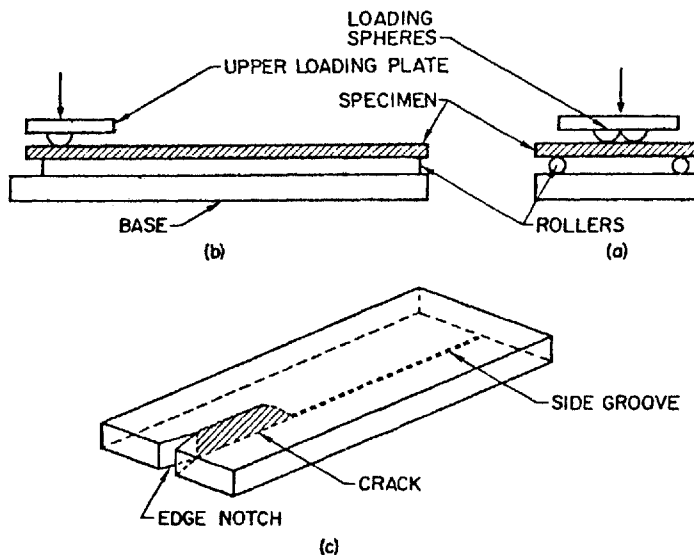


Figure 6.2: Double Torsion Testing Arrangement. Crack profile is shown (Evans, 1972).

A major difficulty with the technique is to ensure that mode I cracking occurs (Evans, 1972; Murray et al., 1975) because if the crack front is parallel to the direction of loading then failure would occur due to shear stresses and correspond to mode III. It has been shown (Evans, 1972; Trantina, 1977; Virkar and Gordon, 1975) that a propagating crack has a curved front which extends further along the lower face of the specimen (Figure 6.2) and this suggests that the crack propagation direction is nearly parallel to the loading direction. Evans (1972) also showed that the fracture toughness value of a glass (for which  $G_{IIIC} \gg G_{IC}$ ) which was established by a DT test agreed well with  $G_{IC}$  values found by other techniques and this suggests that mode I is the predominant mechanism of cracking.

A few features of the double torsion test are also valid for other fracture mechanics tests. For example the specimen can be grooved on one or both sides as an aid to the direction of crack propagation. Generally the stability of cracking depends on cracking conditions given by equation 6.15 and the geometrical shape of the test piece. Both of these factors are considered in the geometric stability factor (gsf) (Yamini and Young, 1977; Mai et al., 1975; Mai, 1974; Clausen, 1969; Gurney and Mai, 1972) and the specimen geometry is more stable against cracking for the more negative gsf.

#### 6.4.2 Experimental

Some experiments were conducted on sprayed coatings using the DT test since crack propagation proceeds at a constant stress intensity, which facilitates the processing of data to establish the critical strain energy release rate. The specimens were prepared from 150 mm x 5 mm mild steel substrates 20 mm thick and the substrate edge was grit blasted with alumina immediately prior to spraying. Only flame sprayed deposits, which were prepared according to the commercially recommended spraying schedule (Table 4.1d), were tested by the DT method.

A support bar with the same dimensions as the specimen with its edge grit blasted and then degreased was attached to the coating using an epoxy adhesive. The bar was spaced 1-2 mm from the specimen and a mould formed around the joint with either aluminium foil or adhesive tape. The adhesive (Araldite D with hardener HY951) was carefully prepared to avoid air or moisture entrapment during the subsequent handling so that a defect free, tough bond layer could be cast. The adhesive was mixed and degassed under vacuum for 15 minutes prior to pouring into the mould; and then degassed for a further 15 minutes. After a 5-7 hour cure at 40°C the excess adhesive was trimmed away and both sides machine-ground without lubricant. For most tests both sides of the specimen were grooved by surface grinding to a depth of 1 mm along the coating-substrate interface.

For the DT test used in this investigation the initial 10 mm length of the coating was tapered so that the crack, which was started from a sawcut (0.2 mm thick) at the leading edge of the coating taper, gradually grew to the full width (about 5 to 6 mm) of the specimen. The DT tests (Figure 6.3) were carried out in an Instron universal testing machine at a cross-head speed of  $2.5 \times 10^{-5} \text{ m min}^{-1}$  and the load vs cross-head displacement curve recorded. The critical stress intensity factor is given by equation (6.17) where the Poisson ratio for alumina is about 0.25. The critical strain energy release rate was calculated from the  $K_{IC}$  data in conjunction with relation (6.13) which has been modified for plane stress conditions:-

$$G_{IC} = \frac{K_{IC}^2}{E} \quad \dots (6.18)$$

The Young's modulus (E) was estimated from the bulk properties of alumina as  $3.45 \times 10^{11} \text{ Pa}$ .

During the progress of the investigation it became apparent that the nature of crack propagation should be examined in order to determine whether coating failure occurred by mode I cracking. An electrical resistance technique was devised whereby electrical conductors were pointed across 6 different locations of the expected crack path (Figure 6.4).

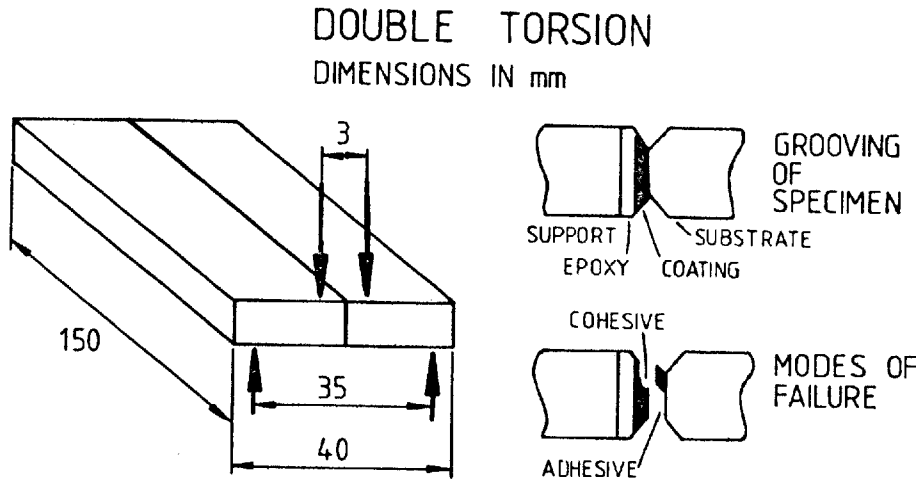


Figure 6.3: Double torsion geometry and testing configuration. Types of failure are referred to in section 6.4.3.

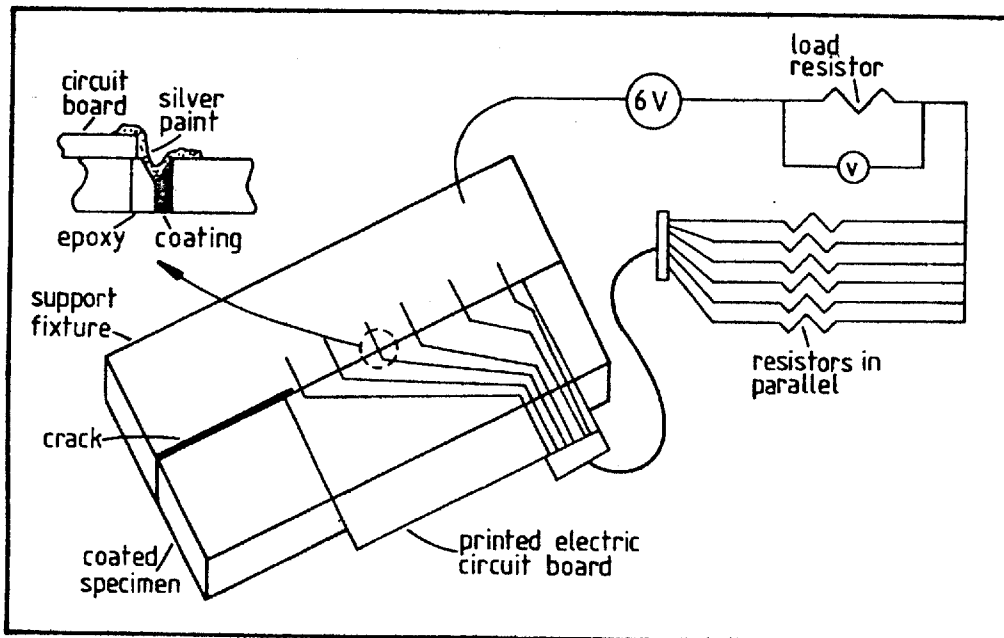


Figure 6.4: Electrical resistance method of following the crack growth. Inset shows the conducting strips painted across the expected crack path.

Each electrical path incorporated a resistor and these were combined into a parallel circuit with a 6 volt supply. The load resistor was in series with the other resistors and its voltage drop can be used to determine the position of crack advancement. When carrying out these measurements thin milar sheets were placed on the rollers of the DT rig so that the specimen was electrically insulated.

The fracture surfaces of selected samples were examined by scanning electron microscopy.

#### 6.4.3 Results

The results of the DT tests are summarised in Table 6.1 and typical force-displacement curves are illustrated in Figure 6.5.

Table 6.1: Results of Double Torsion Tests

| Specimen No. | $K_{IC}$<br>( $\times 10^6$ ) $Nm^{-3/2}$ | $G_{IC}$ ( $J m^{-2}$ ) | Type of Failure |
|--------------|-------------------------------------------|-------------------------|-----------------|
| 17           | 5.35                                      | 83                      | 1               |
| 18           | 4.04                                      | 47                      | 2               |
| 19           | 3.42                                      | 34                      | 2               |
| 20           | 5.58                                      | 90                      | 1               |
| 21           | 6.41                                      | 119                     | 1               |
| 22           | 4.51                                      | 59                      | 1               |
| 23           | 3.87                                      | 43                      | 1               |
| 26           | 3.15                                      | 29                      | 2               |
| 27           | 3.04                                      | 27                      | 2               |

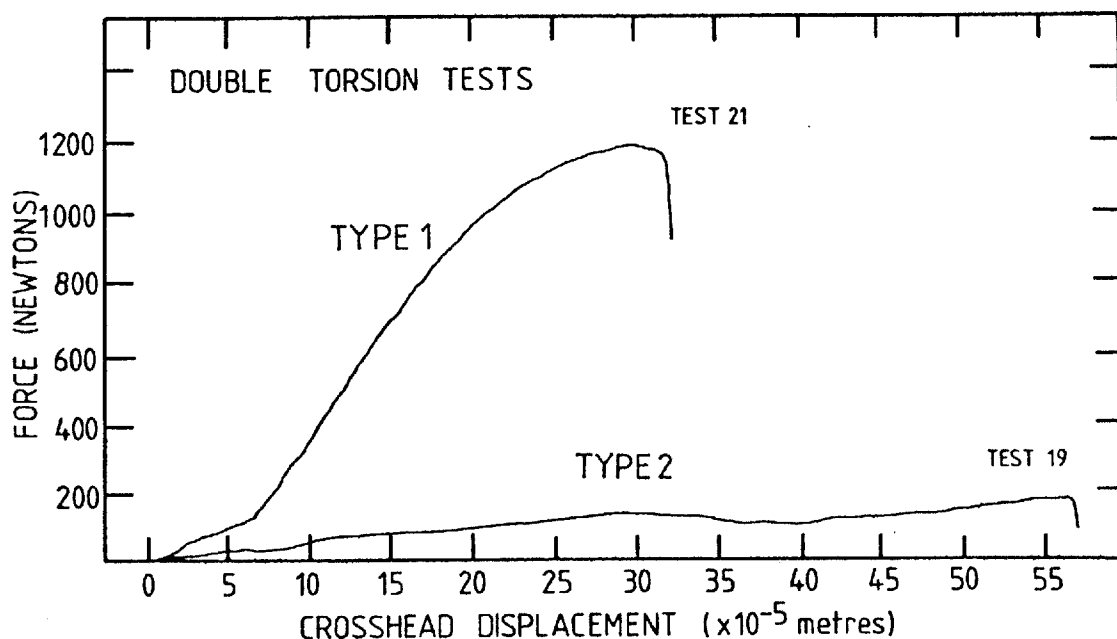


Figure 6.5: Typical force-displacement curves for DT tests.

Two types of behaviour could be distinguished, type 1 in which load increased to a maximum with only a short constant load regime and type 2 which showed the classical result for the DT test with a constant load region for a large part of the crack propagation. The critical load for crack propagation was taken as the maximum for type 1 failure; this gave higher values of fracture toughness than specimens which failed by type 2. Examination of the fracture surfaces showed that type 1 failures generally initiated within the adhesive and changed to within the coating after the crack had progressed 10-30 mm. The abrupt change in crack path is indicated by the sudden load drop and the values obtained are therefore not representative of the coating properties.

Failure did not occur within the adhesive for type 2 but the crack followed a mixed adhesive-cohesive morphology with the cohesive mode dominating where there were compressive forces in the specimen (Figure 6.3). The fracture toughness value thus incorporates both an adhesive and cohesive component and is of limited usefulness.

Figure 6.6 shows the fracture surface of an alumina coating sprayed onto a grit blasted mild steel substrate. The alumina particles were not significantly deformed by impact against the substrate during spraying and, as already noted in section 4.3, dendritic artefacts were exhibited on the fracture surface. The coating was consequently very porous and the adhesive penetrated to the locus of failure and formed features on the substrate which had the appearance of craters. Thus the coating had a high porosity and the DT test does not solely represent the coating properties since failure also occurred within the adhesive.

The crack propagation studies did not show the distinct voltage increases that were expected of a running crack since the conducting paint did not break abruptly at the small deflections of the DT specimen (maximum of 0.5 mm) but necked and remained conducting. It is most probable that the crack initiated in the tensile region of the specimen and propagated parallel to the loading direction so that the two halves of the specimen deformed like a hinge.

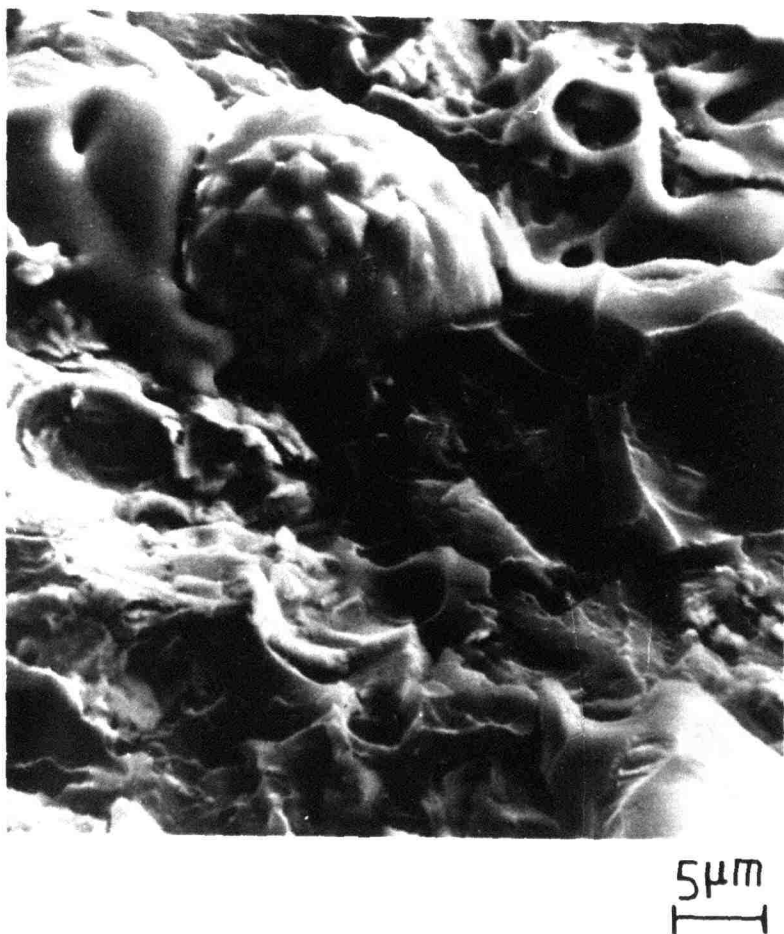


Figure 6.6: Fracture surface of DT specimen.

#### 6.4.4 Discussion

Although, in principle, the DT technique has the advantage that it is only necessary to measure the maximum load during a test to determine the fracture toughness, the present results suggest that it is not suitable for measurements on coatings because of difficulties with control of the fracture path.

Figure 6.5 shows two types of failure for the DT test. Type 1 represents initial failure through the organic adhesive. Failure may initiate in the adhesive if a local stress concentration is produced by a sharp microcrack which may be accidentally introduced during the precracking operation. In a similar manner the stress concentration in the adhesive may be greater than that in the coating if there is a slight misalignment of the specimen in the DT apparatus.

The force reaches a higher value than for failure through the coating since the adhesive has a much greater fracture toughness than the coating. When the crack begins to propagate through the adhesive, which is indicated by the part of the force-displacement curve which levels off, it will tend to move towards the material which has a lower fracture toughness - i.e. the coating. When the crack does enter the coating after about 10 to 30 mm then failure, represented by the vertical section of the force-displacement curve, occurs instantaneously because the stress level is in excess of the value that the coating can withstand.

Type 2 failure occurred entirely within the coating and crack propagation initiated in the horizontal section of the force-displacement curve in Figure 6.5 at approximately  $29 \times 10^{-5}$  m. The vertically decreasing section of the curve at  $57 \times 10^{-5}$  m represents complete failure of the specimen. The morphology of cracking as indicated in Figure 6.3 is mixed; with adhesive occurring on the tensile force side of the specimen and cohesive on the compressive force side of the specimen. Therefore the DT test is limited since it cannot be used to differentiate between adhesive and cohesive fracture energies.

It could also be argued on the basis of the fracture studies that the crack does not propagate under tensile loading conditions but moves from the tensile edge to the compressive edge - a total propagation distance of 5 mm. Some crack propagation experiments were carried out but even though these were unsuccessful it is probable that the final failure of the specimen occurs under shear forces. Thus the DT test produces an oblique fracture across the coating thickness as a result of the stress patterns arising from the four point loading arrangement. Increased sensitivity with more control over the crack path may be obtained by altering the geometrical arrangement of the loading points and the specimen design. Thus the relative angle at fracture across the specimen could be decreased and this would change the localised stress distribution in such a way that either wholly cohesive or adhesive failure occurred. It should be remembered that the analysis of the DT configuration assumes that the end of the specimen is built in and the crack

propagation studies show that this is certainly not the case for the adhesive joint described. In fact, the true DT stress pattern would only be achieved if the free end was clamped.

The main purpose of the groove is to locally reduce the cross-sectional area in the region of the coating so that this material cracks in preference to the adhesive. The groove root radius does not affect the crack propagation since there would be natural microcracks already within the coating from which failure would initiate.

The DT test with type 2 failure as shown in Figure 6.5 takes approximately 23 mins. to carry out at a cross-head displacement rate of  $2.5 \times 10^{-5} \text{ m min}^{-1}$ . Crack propagation commences at  $29 \times 10^{-5} \text{ m}$  (the beginning of the horizontal portion in Figure 6.5) so the crack propagates the length of the specimen (140 mm since there is a 10 mm precrack) in 11 mins. which is an average rate of  $\frac{140 \times 10^{-3}}{11} = 1.3 \times 10^{-2} \text{ m min}^{-1}$ . Therefore the average speed is much greater than the displacement rate - as expected. It should be noted that the same calculations may also lend support to the theory of crack propagation through the specimen thickness where a crack speed of  $\frac{5 \times 10^{-3}}{11} = 4.5 \times 10^{-4} \text{ m min}^{-1}$  is found.

Thus the values of the coating fracture toughness are limited because:

- (i) the values represent a mixed adhesive-cohesive fracture mode;
- (ii) failure has not occurred under tensile loading but due to shear loading through the thickness of the specimen.

Neither of these assumptions are inherent in the DCB test which is described in the following section (6.5).

## 6.5 DOUBLE CANTILEVER BEAM TESTS

### 6.5.1 Literature Survey

#### 6.5.1.1 Principles of Double Cantilever Beam Tests

The double cantilever beam (DCB) and DT specimens both have a rectangular geometry but the stresses that are pre-requisite for mode I cracking are obtained in a different manner. There are a number of ways of loading a DCB specimen, Figure 6.7 (Lawn and Wilshaw, 1975, pp. 57-65; Freiman et al., 1973; Ripling et al., 1964; Srawley and Gross, 1967). The equations (6.19 to 6.22) used to find the strain energy release rate are much simplified and have not accounted for deformation at the edges and ends of the specimen.

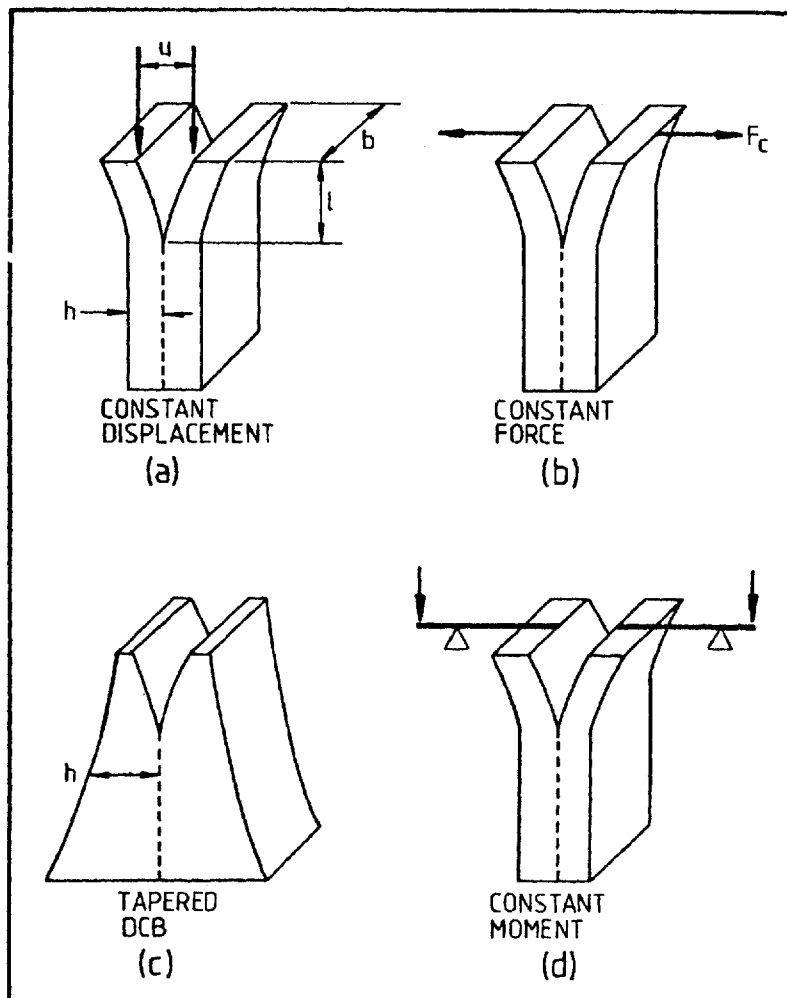


Figure 6.7: Double cantilever beam test pieces. The parameters are referred to in the text.

## (1) Constant Displacement Conditions

$$G = \frac{3 E \mu^2 h^3}{16 \ell^4 b} \quad \dots (6.19)$$

where  $G$  = strain energy release rate ( $\text{J m}^{-2}$ )  
 $E$  = Young's modulus of material ( $\text{Nm}^{-2}$ )  
 $\mu$  = total displacement (m)  
 $h$  = specimen arm height (m)  
 $\ell$  = crack length (m)  
 $b$  = specimen width (m).

## (2) Constant Force Conditions

$$G = \frac{12 F^2 \ell^2}{E h^3 b} \quad \dots (6.20)$$

where  $F$  = force (N).

## (3) Tapered DCB Geometry

$$G = \frac{4 F^2}{b E} \left[ \frac{3 \ell^2}{h^3} + \frac{1}{h} \right] \quad \dots (6.21a)$$

where  $h$  = specimen arm thickness (m) at crack length  $\ell$ .

## (4) Constant Moment Conditions

$$G = \frac{12 M^2}{E h^3 b} \quad \dots (6.22)$$

where  $M$  = moment arm (N-m)

The expressions for the strain energy release rate of the experimental configurations shown in equations 6.19, 6.20 and 6.21a include a term for the crack length. This can easily be found during the progress of the experiment for a transparent material by direct measurement but for an opaque material on indirect means must be used. Usually a compliance calibration is carried out; where the relative deflection between the specimen arms is found in relation

to various artificial crack lengths (Knott, 1976, pp. 105-106; Davidge and Tappin, 1968).

From equation (6.21a) it can be seen that the crack length for the tapered DCB specimen must be known in order to find the strain energy release rate. If the beam arms are contoured so that the compliance changes linearly with the crack length then the expression :-

$$\frac{3 \ell^3}{h^3} + \frac{1}{h} \quad \dots (6.21b)$$

is a constant and the relation between the load and strain energy release rate is independent of the crack length. The specimen is said to have constant K characteristics and the critical strain energy release rate ( $G_{IC}$ ) varies only with the critical force ( $F_C$ ). Likewise if the taper angle of the DCB specimen is sufficiently small then the specimen geometry approaches that of constant K properties. Much work has been carried out on the stability of tapered DCB specimens (Mai et al., 1975; Mai, 1974; Clausen, 1969). Generally, as in the case of the parallel sided DCB, the gsf of tapered specimens under constant displacement conditions is much lower than for constant loading conditions. However the cracking stability increases with taper angle for load controlled systems whereas the stability decreases with taper angle for displacement controlled systems. The constant moment specimen (Figure 6.7d) also has constant K characteristics and will be discussed in section 6.5.1.2 in relation to the testing of coatings.

#### 6.5.1.2 Experimental Details

The DCB geometry with both parallel and tapered arms has been used extensively in measuring the fracture toughness of adhesive joints (Trantina, 1972; Mostovoy et al., 1967; Ripling et al., 1964; Gurney and Amling, 1969; Anderson et al., 1977). The adhesive is incorporated into a sandwich structure so that the DCB arms (usually manufactured from aluminium) lie on either side of the

adhesive layer. Thus the coating forms part of an adhesive joint and failure is restricted to within the coating or at the substrate-coating interface. The fracture toughness parameters of the coating ( $G_{IC}$  and  $K_{IC}$ ) can then be estimated by assuming that energy to the failure process is contributed from the elastic bending of the specimen arms so that equations of the form 6.19 to 6.22 are valid.

This approach has been used to study the effect of firing conditions on the adhesion of thick film conductors to alumina substrates (Becher and Newell, 1977). The applied moment DCB technique was used since no crack length measurement is needed in order to determine the critical strain energy release rate. The specimens (Figure 6.8) consisted of thick film Pt-Au strips (2.0 mm wide x 19.1 mm long) which had been screen printed onto alumina substrates (25 mm x 25 mm x 0.6 mm). The loading fixture which enabled removal of the coating was not attached with an organic adhesive, as described for adhesive joints, but the specimens were dip soldered (0.05 to 0.13 mm thick) so that a brass cantilever arm could be attached.

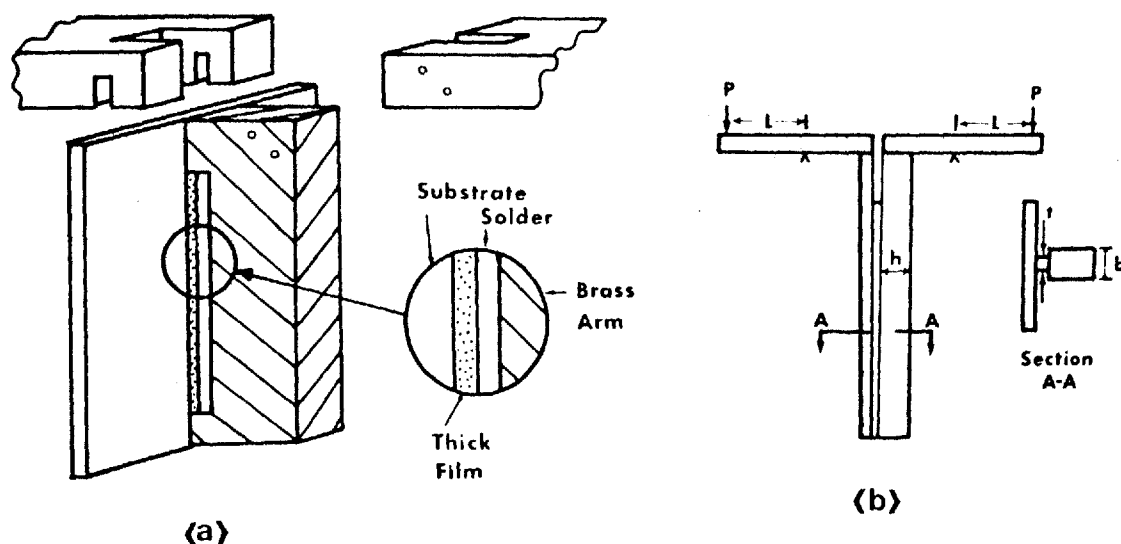


Figure 6.8: Applied moment DCB specimen for measuring the adhesion of thick films (from Becher and Newell, 1977).

- (a) specimen preparation
- (b) testing arrangement.

An alumina backing substrate (1.3 mm x 25 mm x 25 mm) was then added and the assembly slotted into standard loading arms. The calculation of the critical strain energy release rate ( $G_{IC}$  in units of  $J m^{-2}$ ) for this non-symmetric sample must consider the strain energy in the brass and alumina arms. Thus:-

$$G_{IC} = \frac{12 M^2}{EI} \quad \dots (6.23a)$$

$$= \frac{M^2}{2b} \left| \frac{12}{E_1 I_1} + \frac{12}{E_2 I_2} \right| \quad \dots (6.23b)$$

where  $M$  = applied bending moment (N-m)

$b$  = crack plane width of coating (m)

$I$  = moment of inertia ( $m^4$ )

$E$  = Young's modulus (Pa).

Subscript 1 = brass

Subscript 2 = alumina.

If the strain energies of each arm are not comparable then the crack will have a tendency to move towards the arm with the highest strain energy and the fracture toughness will not be representative of the bulk material.

Two modes of failure were distinguished in relation to the fracture surface energy and the temperature of firing. Samples which had been fired at  $860^\circ C$  failed in the glassy layer between the metal coating and substrate with a total free energy of  $3.6 J m^{-2}$  and were termed cohesive. At firing temperatures greater than  $1000^\circ C$  the samples failed in an adhesive manner at the glass/metal interface with a comparatively low critical fracture energy of  $0.5 J m^{-2}$ . At intermediate firing temperatures there was a change in the failure mode and the critical free energy.

The bulk properties of the materials give some indications of how the stress intensity factor would be expected to change across an interface (Good, 1972), but in practice (Becher et al., 1978) the stress intensity factor varied according to the penetrating nature of the glass at the metal-glass interface (Figure 6.9). Since the

glass phase has the lower fracture toughness than the maximum adherence was achieved when the glass layer has the least resistance to failure (i.e. curve "a" figure 6.9); and this corresponded to cohesive failure. On the other hand for process conditions that promoted a smooth glass/metal interface the fracture toughness was minimum and adhesive failure occurred.

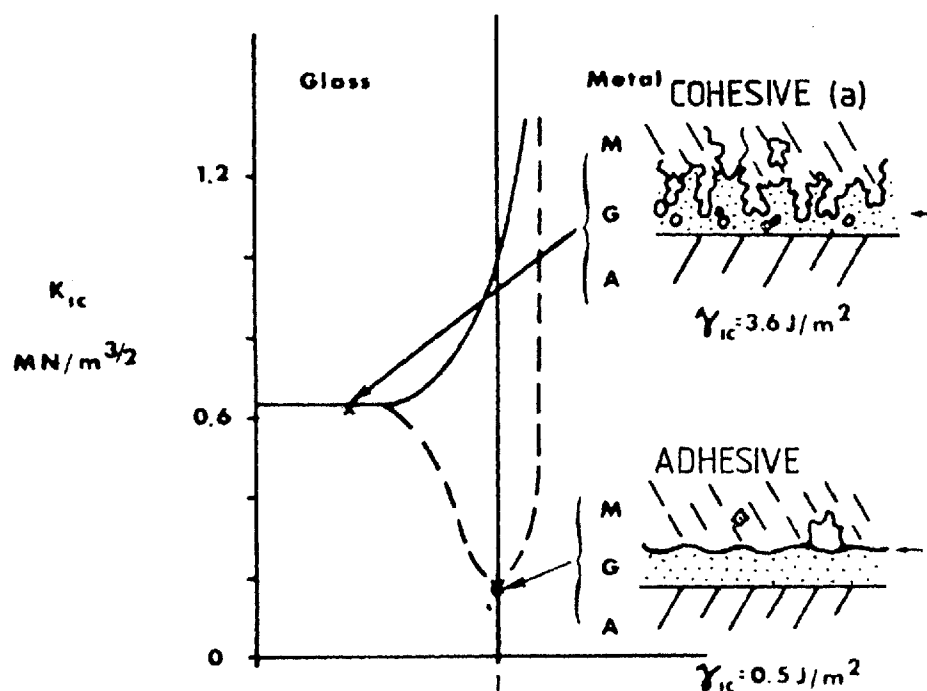


Figure 6.9: Model of stress intensity profile through film and substrate. (Becher et al., 1978).

Thick film metallisations were also tested using the DCB geometry in which one arm was contoured Figure 6.10 (Bascom and Bitner, 1977). The stress distribution at the crack tip was assymetric and the crack front was directed into the film which made this test more sensitive to differences in film morphology. The experimental fracture toughness values exhibited a wide scatter that fitted a normal Gaussian distribution which in some cases was bimodal. No differences in the fracture morphology were discerned for the samples which had two characteristic fracture toughness values. It was proposed that micro-cracking processes that take place near the crack tip controlled the fracture toughness. If

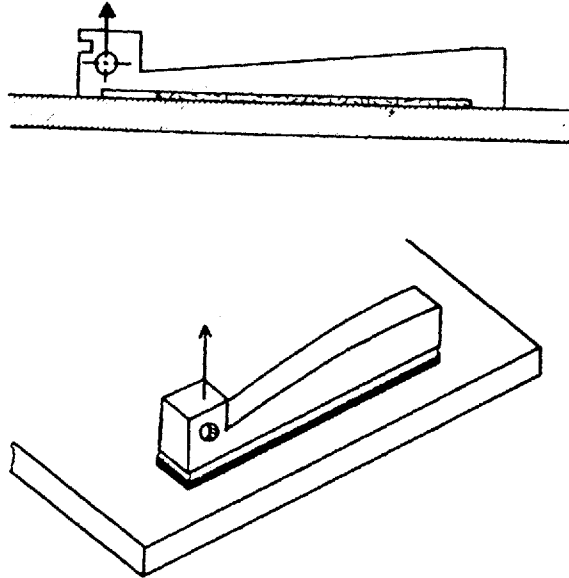


Figure 6.10: Specimen with DCB geometry in which one arm is contoured (Bascom and Bitner, 1977).

extensive micro-cracking takes place ahead of the crack tip then the fracture toughness value was high compared to a process that occurred in the near vicinity of the crack tip; and in both cases the fracture morphology appeared similar. The statistical analysis enabled the collection of many experimental results which inferred different mechanisms for crack growth; even though no marked variation in the fracture morphology was observed.

Elssner and Pabst (1974, 1975) and Pabst and Elssner (1980) used a single edge-notched specimen under four point loading (Figure 6.11) to test the solid state bonding of niobium metal (about 0.5 mm thick) to alumina at temperatures less than 1600°C. The stress intensity factor was evaluated from a standard formula and used to discriminate between the various fracturing processes. The fracture followed three distinct paths (Elssner et al., 1975):

- (1) Failure within the thin metal layer occurred at a representative stress intensity factor of  $3.5 \times 10^6 \text{ Nm}^{-3/2}$ .
- (2) Failure within the ceramic part of the bond zone was

observed for materials with a high porosity. The fracture toughness value of  $2.4 \times 10^6 \text{ Nm}^{-3/2}$  was greater than that of the ceramic by itself ( $0.7 \times 10^6 \text{ Nm}^{-3/2}$ ), and this is indicative of a strengthening effect by either penetration of the metal phase or the high temperature heat treatment of the ceramic.

- (3) Failure in the metal/ceramic interface zone. The fracture toughness value (about  $3.4 \times 10^6 \text{ Nm}^{-3/2}$ ) did not change significantly for several alumina ceramics of varying purity and the ceramic fracture surface did not exhibit any plastic deformation.

It should be noted that fracture toughness values greater than the as received material were measured because the loading arrangement allowed higher local stresses in the region of interest and these were accentuated by notching. Thus Elssner and Pabst (1974, 1975) and Pabst and Elssner (1980) quantitatively assessed metal/ceramic joints and related the failure mechanism to processing and material variables.

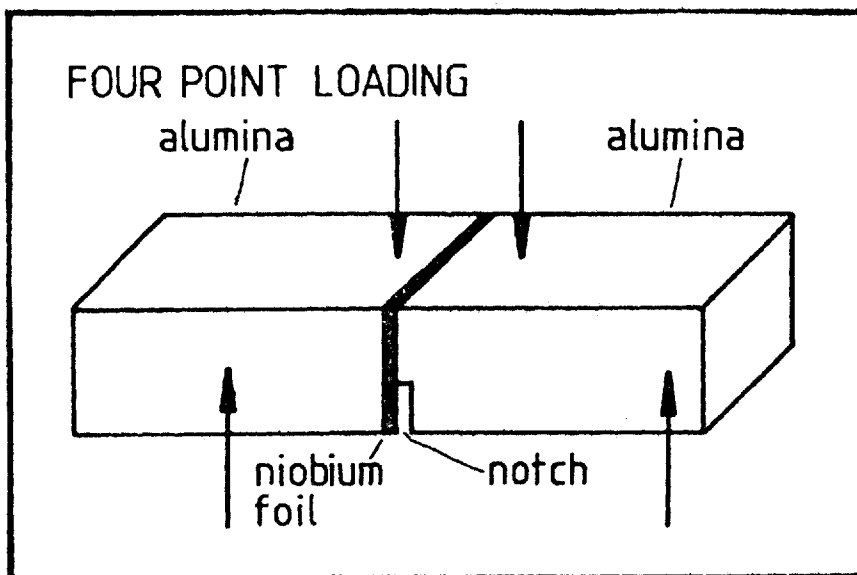


Figure 6.11: Four point bending arrangement to test coating adhesion (Elssner and Pabst, 1974).

### 6.5.1.3 Discussion

The adhesion of a coating to a substrate can be measured by carrying out a modified fracture mechanics test but several aspects of the test must be considered to ensure that it is representative of the material properties and not a function of the testing variables. The energy dissipated during the cracking process is strongly dependent on the area of the crack tip and the original Griffith equation (equation 6.1) used to find the fracture toughness value assumes that the tip of the propagating crack has dimensions approaching that of inter-atomic spacing. This condition may not be valid, especially during the commencement of a fracture toughness test where an initial crack (termed a pre-crack) must be introduced into the material. Natural pre-cracks can usually be made (Evans, 1974) by fatigue cracking or pre-stressing the specimen; but invariably an artificial pre-crack is made by sawing a fine slot (0.1 - 0.2 mm wide) with a jewellers saw (Pabst, 1974).

If the specimen configuration is such that many toughness values can be obtained by examining the force required to change the crack length, then the results of the first loading operation can be discounted and the test used only to establish a sharp pre-crack. Alternatively the effect of the pre-crack root radius can be accounted for by carrying out a large number of tests (Pabst, 1974) for various root radii. The approach may not have to be as rigorous for materials with a highly inhomogeneous structure. For example, if the coating was highly porous or already contained a high number of cracks then some of these features would be expected to extend from the artificial pre-crack and give an effective pre-crack approaching atomic dimensions. Alternatively it could be argued that a natural pre-crack would be limited to a scale of events determined by the porosity or any pre-existing flaws. Thus for a highly inhomogeneous structure it may not be necessary to pre-crack the specimen in such a way that a crack in accordance with the Griffith criterion is produced.

As a crack extends there is a set relationship between the crack length, applied force and compliance of the specimen which is normally expressed in terms of the equation:-

$$G = \frac{F^2}{2b} \frac{dC}{d\ell} \quad \dots (6.24)$$

The energy change as a crack grows can be illustrated according to Figure 6.12. When the crack grows from length  $\ell$  to  $(\ell + \delta\ell)$  the crack area changes from  $A$  to  $(A + \delta A)$  with corresponding changes in the force  $F$  to  $F + \delta F$  and compliance  $(\mu/F)$  to  $(\mu + \delta\mu/F + \delta F)$ . The area enclosed within the triangle

$$[(0,0) - (\mu, F) - (\mu + \delta\mu, F + \delta F)] \quad \dots (6.25)$$

represents the energy change for a crack to grow an increment  $\delta\ell$ . Therefore the crack extension force per unit crack length can be found from the relation :-

$$G = \frac{A_1}{2 b \delta\ell} \quad \dots (6.26)$$

where  $A_1$  = area enclosed within the force vs displacement curve (J)  
 $b$  = width of specimen (m)  
 $\delta\ell$  = increment of crack growth (m)

This method of finding the fracture toughness of a material is termed the "work of fracture method" (Davidge and Tappin, 1968) and is only applicable where cracking is stable. Thus when the load is removed from the specimen the crack should stop running and the unloading curve correspond to the compliance of the new crack length.

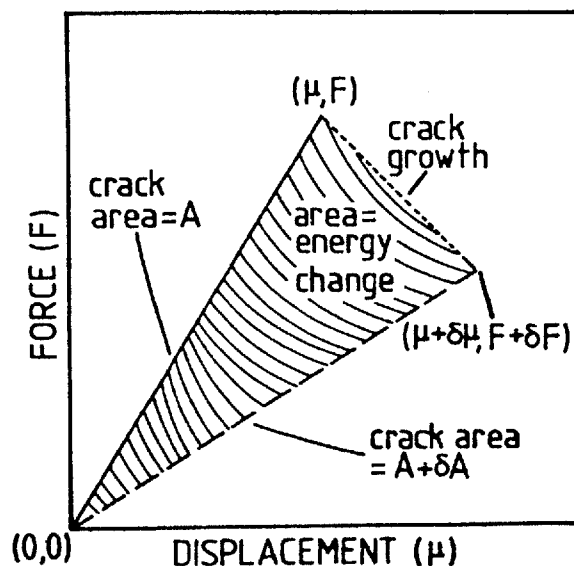


Figure 6.12: Energy change when a crack grows.

The above graphical technique is not suitable for materials or testing methods where the specimen fails catastrophically, such as in the case of ceramic materials under three point bending (Davidge and Tappin, 1968). The stable cracking properties of the DCB geometries would be expected to lend themselves to this analysis.

A major problem associated with the DCB test, where the specimen is manufactured as a composite of several materials, concerns the different mechanical properties of the various components on the specimen compliance. For example in the cases of the applied moment DCB (Becher and Newell, 1977) and contoured single beam test (Bascom and Bitner, 1977), which have been described in section 6.5.1.2, the loading fixture is soldered to the coating and any role of this layer (the solder) in contributing energy to the cracking process must be accounted for. In the above cases plastic or elastic deformation of any interlayers was considered negligible and thus they were not included in the overall thickness of the specimen geometry. However for other tests where the bonding layer is relatively thick or has different material properties from the loading fixtures it is necessary to evaluate the effect on the compliance measurement.

## 6.5.2 Compliance Measurements

### 6.5.2.1 Introduction

Examples of tests have been described in section 6.5.1 where the adhesion of thin films and coatings to a substrate has been tested by attaching a loading fixture to the coating. The loading fixture is termed an adherend and its removal, together with the coating, gives a measure of the coating fracture toughness.

However prior to carrying out tests on coatings it is necessary to calibrate the specimen so that the crack length can be measured indirectly. The deflection vs force properties of the specimen vary with the crack length and these properties do not change according to the theory of an ideal cantilever beam because

corrections for bending and shearing of the beam at the crack tip must be taken into account. Thus the rigidity of the specimen for a range of crack lengths must be experimentally determined and the inverse of this (i.e. displacement/force) is termed the specimen compliance. If the specimen compliance and crack length are known then the expression  $dC/d\ell$  can be evaluated and the strain energy release rate determined via equation 6.24. The compliance calibration is therefore important and must be carried out with care.

The geometry of the DCB specimens used in the compliance measurements (section 6.5.2) and the testing of coatings (section 6.5.3) was approximately the same as the samples used for the DT tests (section 6.4). Essentially the only difference in the test procedure was that the cantilever arms were loaded in tension through loading holes in the arms and the displacement was measured by an extensometer positioned on the free ends of the cantilever arms. Also, in the case of the compliance measurements, the cantilever arm material was changed to combinations of aluminium and mild steel so that the manner in which the arms deformed could be studied in detail.

In this section three compliance parameters are defined (as below) according to the manner in which the displacement is measured.

- (1) Extensometer compliance ( $C_E$ ) is measured by using the extensometer displacement at the free ends of the cantilever arms. This compliance value cannot be inserted directly into equation 6.24 to find the fracture toughness because the displacement is not measured at the loading points.
- (2) The loading point compliance ( $C_{LP}$ ) is measured at the loading points from the apparent displacement between the grips and can be calculated from the cross-head speed. This compliance value does not take into account the grip compliance; that is the elastic deformation of the grips.
- (3) The true loading point compliance ( $C_{TLP}$ ) is measured by using a specimen which allows an extensometer to be placed at the loading points. In the case of this work the  $C_{TLP}$  was calculated from the extensometer compliance after

the bending behaviour of the cantilever arms had been taken into account.

Therefore the aim of section 6.5.2. is to detail experiments and results which allow the  $C_{TLP}$  to be evaluated so that the fracture toughness of coatings, as presented in section 6.5.3, can be calculated.

A large number of compliance measurements were carried out so the facilities of a digital-analog computer were used to calculate the line of best fit for the force vs displacement data. Thus section 6.5.2.2 describes the experimental arrangement to record the force and displacement data "on-line". Further details of the computer programme are presented in Appendix 4.

#### 6.5.2.2 Data Acquisition

Experimental data from the tensile testing machine (Instron) was collected via the standard recording facilities. In some experiments the electronic signal was continuously monitored and periodically recorded by interfacing the tensile machine with a hybrid computer. Figure 6.13a shows a schematic representation of processing of the load and displacement data. The DC force signal to the chart recorder was amplified 100 times prior to transmission. On the other hand the AC extensometer strain gauge signal was rectified to DC voltage and then amplified via a patchboard network (Figure 6.13b). Both of the analog signals were converted to digital values which were stored for analysis at a later date. The computer programmes that were designed to control this data acquisition system generally sampled a pair of load-displacement readings every  $3 \pm 0.007$  seconds, and typical programmes are given in Appendix 4.

The load cell (cell D used on ranges of 20, 50, 100, 200, 500 pounds) and several extensometers (0 to 25 mm, 100% strain; 0 to 25 mm, 10% strain) were calibrated with respect to their digitised output at various measurements. The equations (Table 6.2)

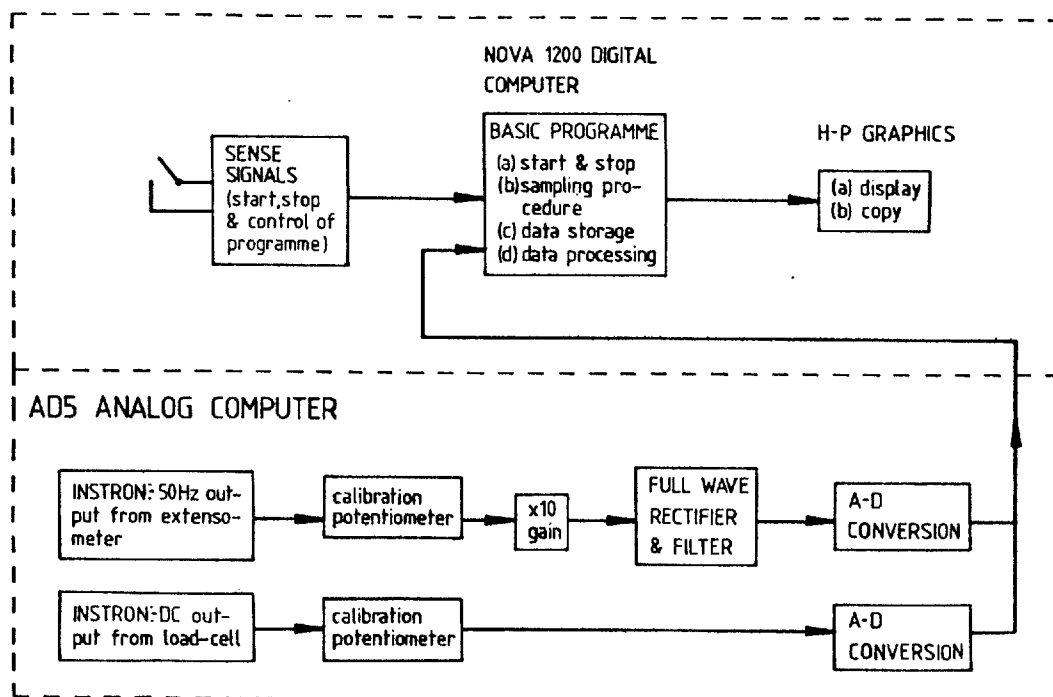


Figure 6.13a: Schematic representation of processing of load and displacement data.

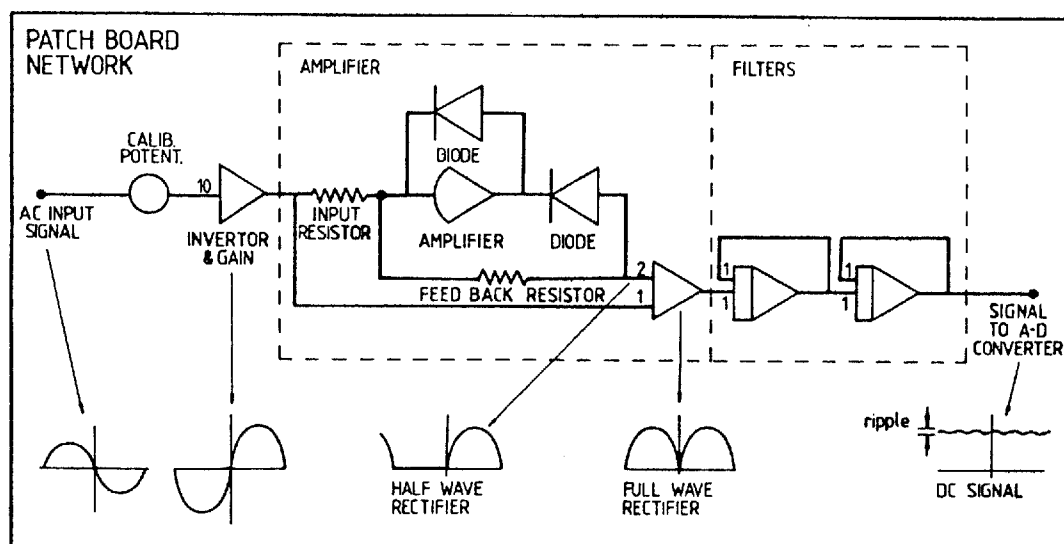


Figure 6.13b: Patchboard network to convert the AC strain gauge signal to a DC signal.

for the calibration curves (Figure 6.14) were derived by standard linear regression analysis.

Equation 6.27 was used to find the force and is accurate to less than 0.5% at the maximum load value.

$$F = 5.132 \times 10^2 \left( \frac{DV \times N}{100} + 8.6 \times 10^{-4} \right) \quad \dots (6.27)$$

where  $F$  = force (N)

$DV$  = digital voltage

$N$  = load cell range (lb)

The digital voltage measurements were accurate to at least  $\pm 0.01V$  which corresponds to sensitivities of  $\pm 1.09 \times 10^{-5} m$  and  $\pm 9.1 \times 10^{-7} m$  for the 0 to 100% strain and 0 to 10% strain extensometers respectively when using range 1. Preliminary results showed that the relative displacement of the DCB arms was in the range of 0 to  $5.1 \times 10^{-4} m$ , and thus the 25 mm gauge length, 0 to 10% strain extensometer was used. The general equation :-

$$\mu = 9.27 \times 10^{-5} (DV \times R_1 + 6.67 \times 10^{-3}) \quad \dots (6.28)$$

where  $\mu$  = displacement (m)

$DV$  = digital voltage

$R_1$  = range

was used to calculate the displacement and is accurate to less than 2% at the maximum displacement value.

Table 6.2a: Load Calibration\*

| Range | Constant<br>A         | Gradient<br>B         | $R^2$ | No. of<br>readings |
|-------|-----------------------|-----------------------|-------|--------------------|
| 20    | $-5.1 \times 10^{-3}$ | $4.33 \times 10^{-2}$ | 1.000 | 3                  |
| 50    | $-2.0 \times 10^{-3}$ | $1.72 \times 10^{-2}$ | 0.999 | 6                  |
| 100   | $-8.6 \times 10^{-4}$ | $8.68 \times 10^{-3}$ | 0.999 | 11                 |
| 200   | $1.5 \times 10^{-3}$  | $4.30 \times 10^{-3}$ | 0.999 | 11                 |
| 500   | $9.0 \times 10^{-5}$  | $1.74 \times 10^{-3}$ | 0.999 | 11                 |

Table 6.2b: Displacement Calibration\*

|                                  | Range | Constant<br>A          | Gradient<br>B          | $R^2$ | No. of<br>Readings |
|----------------------------------|-------|------------------------|------------------------|-------|--------------------|
| 0 to 10% strain<br>extensometer  | 1     | $-6.67 \times 10^{-3}$ | $2.741 \times 10^{-1}$ | 0.999 | 30                 |
|                                  | 2     | $-2.67 \times 10^{-2}$ | $1.376 \times 10^{-1}$ | 0.999 | 30                 |
| 0 to 100% strain<br>extensometer | 1     | $1.29 \times 10^{-2}$  | $2.30 \times 10^{-2}$  | 0.979 | 25                 |

\* equations of the form  $DV = A + BX$

where DV = digital voltage after analog to digital conversion

A = constant which indicates the DV intercept

B = gradient

X = displacement (in 0.001 inches) or,

= load (in pounds)

$R^2$  = coefficient of determination.

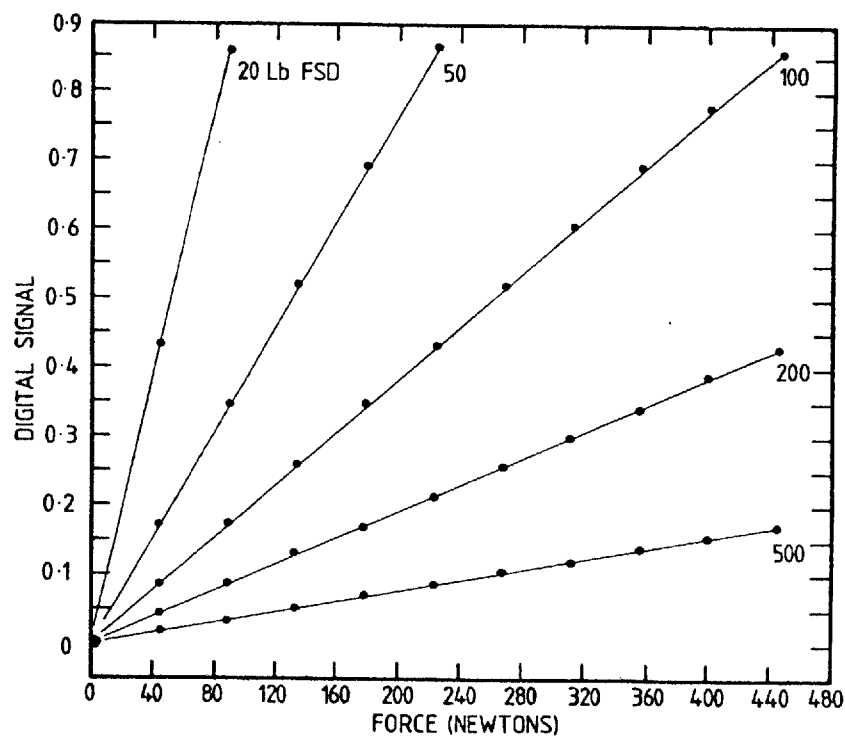


Figure 6.14a: Calibration of load cell with respect to digital signal.

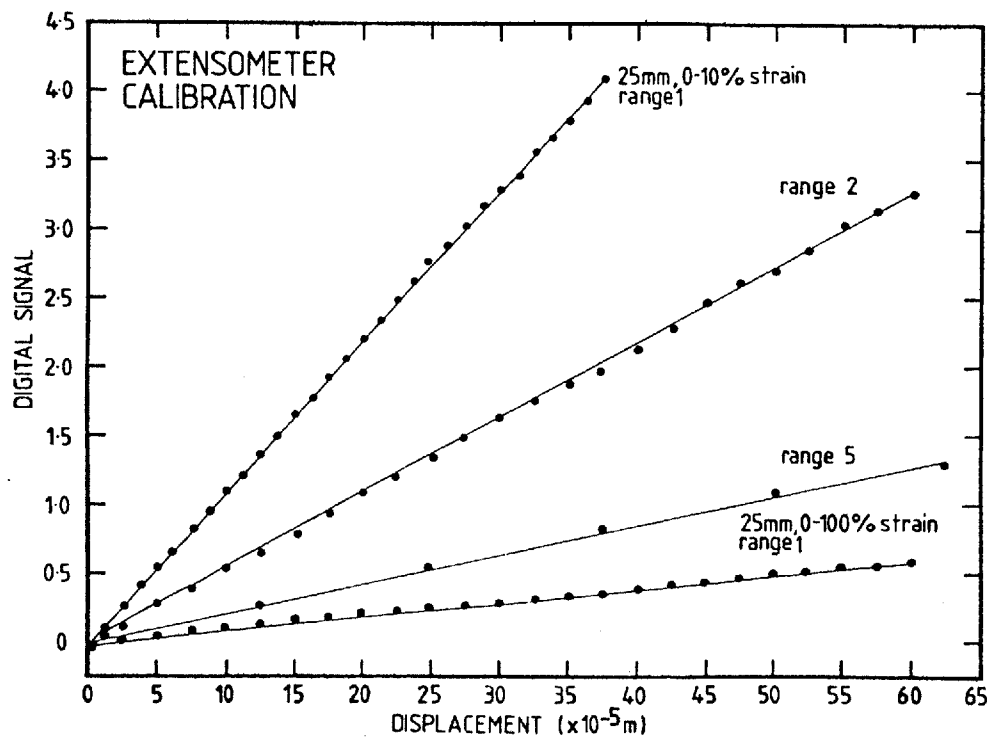


Figure 6.14b: Calibration of extensometers with respect to digital signal.

### 6.5.2.3 Experiments and Results

Several sets of compliance data were obtained. Specimens of the dimensions shown in Figure 6.15, with mild steel arms, were loaded in tension at a cross-head speed of  $1.02 \times 10^{-4} \text{ m min}^{-1}$ . The preparation of these specimens has already been mentioned in section 6.4.2. The relative displacement between the cantilever arms was measured with a 25 mm gauge length, 0 to 10% extensometer. The compliance data for joint thicknesses ranging from 0.5 to 1.5 mm and for grooved and ungrooved specimens all fell on one curve (Figure 6.16) and this fitted an empirical expression:-

$$C_E = 2.108 \times 10^{-4} \ell^{1.989} \quad \dots (6.29)$$

with a coefficient of determination ( $R^2$ ) of 0.989

where  $C_E$  = extensometer compliance ( $\text{m N}^{-1}$ )

$\ell$  = crack length (m)

Another set of compliance measurements were carried out on specimens with adherends of mild steel-mild steel, aluminium-aluminium and mild steel-aluminium, and also the compliance of a mild steel sample (of dimensions 150 x 40 x 6 mm) was determined in the same manner. Data from these tests was obtained according to the methods detailed in the previous section (6.5.2.2) and fitted to linear regression curves to calculate the specimen compliance  $C_E$  (Figure 6.17).

The coefficients of determination for the compliance calculations were typically greater than 0.960 (Table 6.3) and the compliance-crack length curves for the mild steel adherends (Figure 6.17a) held approximately the same relationship as the previous samples (Figure 6.16); as did the mild steel sample. Specimens with aluminium adherends were more compliant than samples prepared from mild steel whereas the sample manufactured with one arm each of mild steel and aluminium had an intermediate compliance to either of these materials alone (Figure 6.17b).

The compliance at the loading point ( $C_{LP}$ ) was calculated from the assumption that the cross-head displacement rate ( $1.02 \times 10^{-4} \text{ m min}^{-1}$ ) was constant and this data is superimposed onto

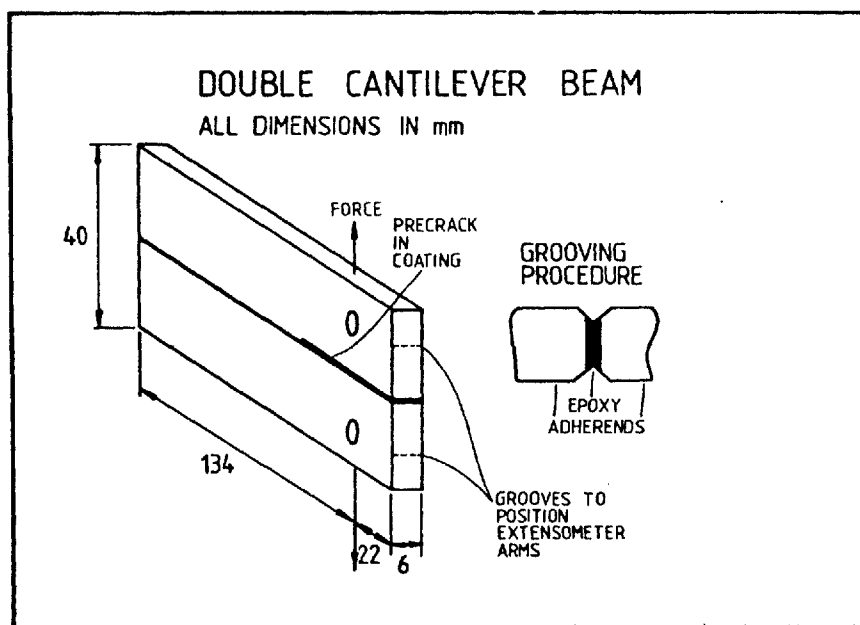


Figure 6.15: DCB specimens used for compliance measurements.

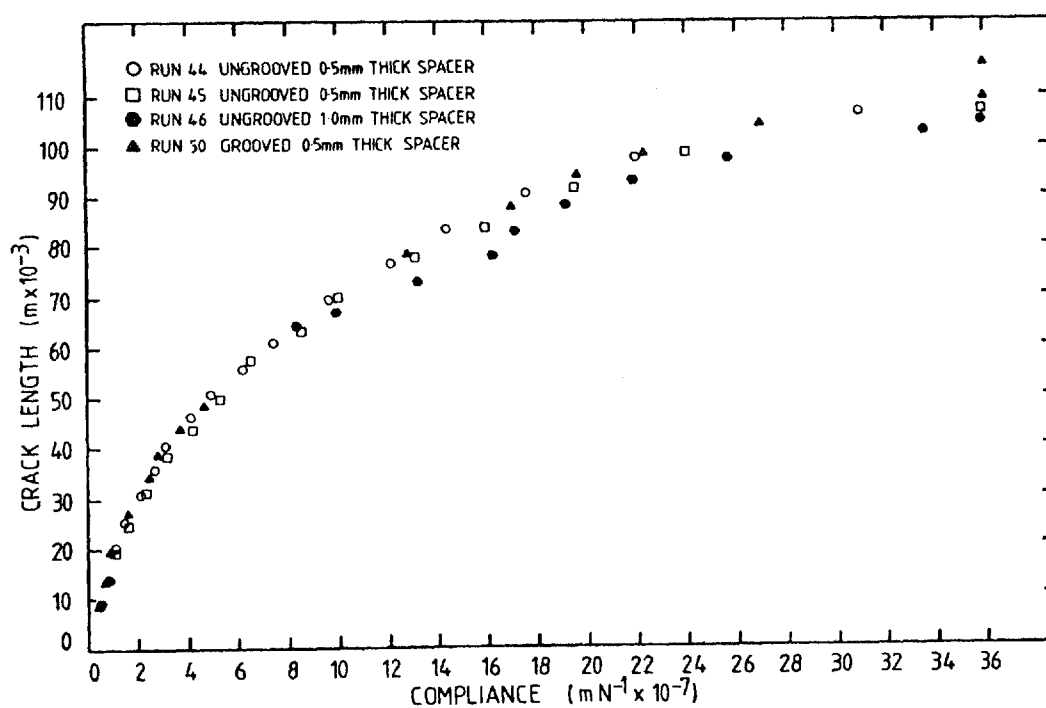
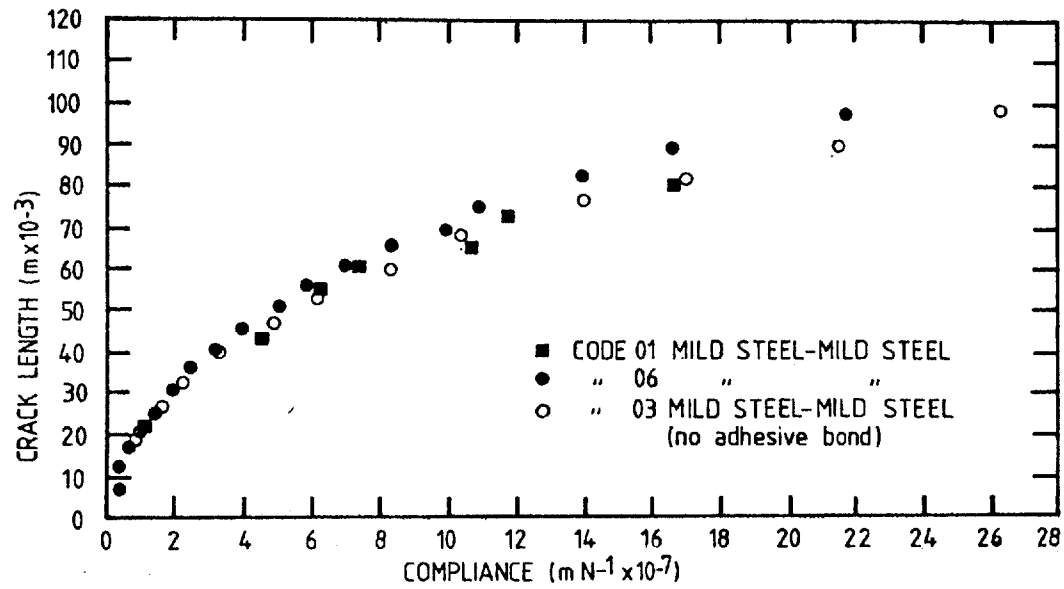
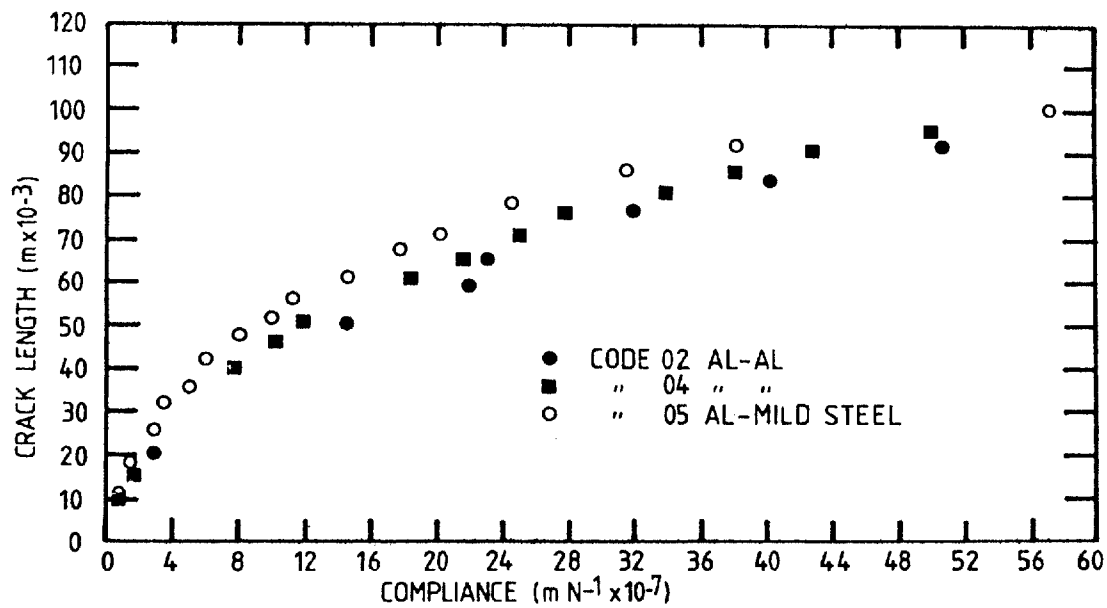


Figure 6.16: Variation of compliance ( $C_E$ ) with crack length for DCB specimens.



(a)



(b)

Figure 6.17: Extensometer compliance ( $C_E$ ) of DCB specimens.

Table 6.3: Lines of best fit for compliance calibrations\*

| Adherends                          | Constant<br>(A) $\times 10^{-4}$ | Exponent<br>(B) | Coefficient<br>of<br>determination | No. of<br>Points |
|------------------------------------|----------------------------------|-----------------|------------------------------------|------------------|
| mild steel-mild steel <sup>+</sup> | 2.108                            | 1.989           | 0.989                              | -                |
| mild steel-mild steel              | 0.935                            | 1.710           | 0.963                              | 26               |
| mild steel only                    | 3.047                            | 2.079           | 0.995                              | 12               |
| Al - Al                            | 3.776                            | 1.868           | 0.989                              | 22               |
| mild steel - Al                    | 3.092                            | 1.897           | 0.978                              | 17               |

\* Equations are of the form

$$\text{Compliance} = A \ell^B$$

where compliance ( $C_E$ ) is measured in  $\text{mN}^{-1}$

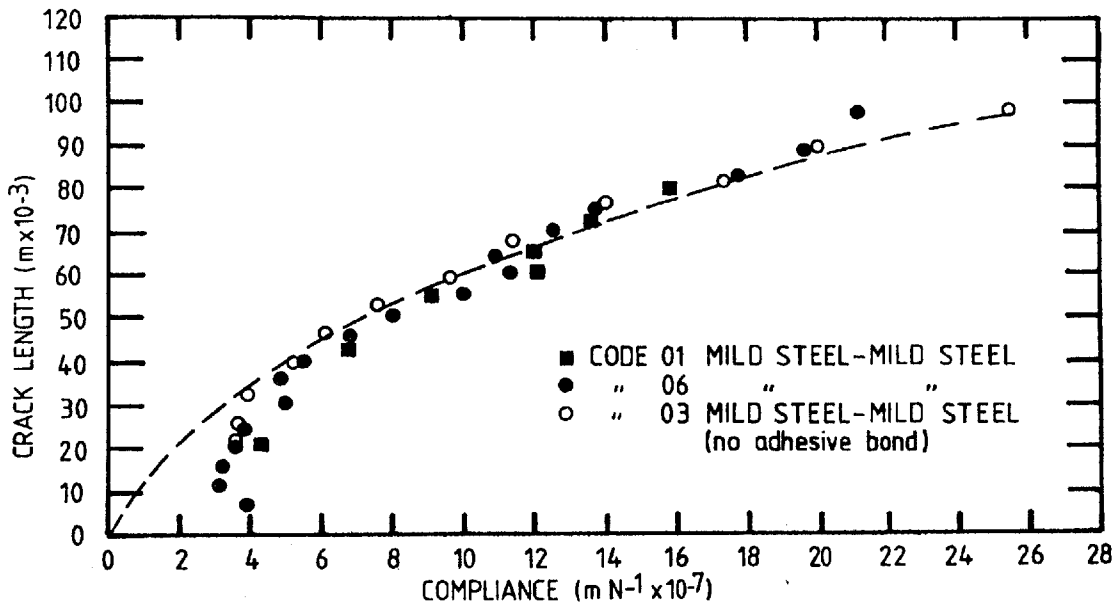
crack length ( $\ell$ ) is measured in m

A and B are constants.

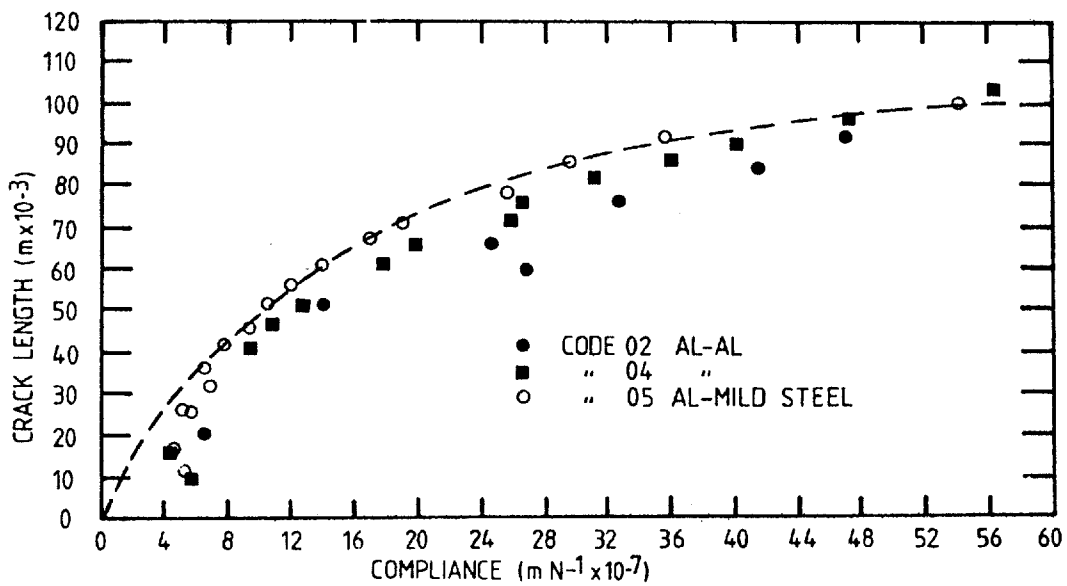
+ Data of Figure 6.16.

the extensometer curves (Figure 6.18). It should be noted that some  $C_{LP}$  values show a significantly greater compliance value than would be expected from the general shape of the graph. For example the first point of sample "06" in Figure 6.18a at a crack length of approximately 5 mm shows a compliance value of about  $4 \times 10^{-7} \text{ m N}^{-1}$  where a value of approximately  $3 \times 10^{-7} \text{ m N}^{-1}$  would be expected. This anomaly arises due to the method by which  $C_{LP}$  was calculated. The displacement term that was used in the compliance expression was calculated directly from the cross-head speed and thus there is the erroneous assumption that the force-deflection curve (at the loading point) is linear. However the loading curve is non-linear; presumably due to factors which can result from:-

- (i) deformation of the adhesive at high loads, or
- (ii) the lack of unavoidable critical alignment of the grips and specimen at low loads.



(a)



(b)

Figure 6.18: Loading point compliance ( $C_{LP}$ ) of DCB specimens.

Thus the displacement value calculated during a period of constant cross-head travel may be overestimated and  $C_{LP}$  will be larger than the true value. Errors were not uniformly normalised due to the requirement of obtaining a large number of force-displacement data pairs which could be used to calculate both  $C_E$  (Figure 6.17) and  $C_{LP}$  (Figure 6.18).

The load point compliance cannot be greater than the extensometer compliance because it is closer to the rotation (or bending) point in the experimental arrangement. Also it would be expected that  $C_{LP}$  would approach zero for decreasing crack lengths. Therefore the true loading point displacement of a mild steel specimen was measured with respect to time (Figure 6.19a). The true loading point compliance ( $C_{TLP}$ ) was calculated and Figure 6.19b shows how the three compliance measurements vary. The true load point compliance values (at four crack lengths) and the actual displacement rates between the loading points are shown in Table 6.4, and it can be seen that the nominal pre-selected cross-head speed of  $1.02 \times 10^{-4} \text{ m min}^{-1}$  is only approached at large crack lengths. The following measurements were made to resolve this apparent discrepancy.

Table 6.4:  $C_{TLP}$  and effective cross-head speed at the loading points

| Crack length<br>$\times 10^{-3} \text{ m}$ | Load Point<br>Compliance $\times 10^{-7} \text{ mN}^{-1}$<br>$C_{TLP}$ | Load Point<br>Cross-head speed<br>$\times 10^{-4} \text{ m min}^{-1}$ |
|--------------------------------------------|------------------------------------------------------------------------|-----------------------------------------------------------------------|
| 17.6                                       | 0.35                                                                   | 0.13                                                                  |
| 39.3                                       | 1.69                                                                   | 0.37                                                                  |
| 59.3                                       | 5.85                                                                   | 0.76                                                                  |
| 89.7                                       | 15.88                                                                  | 0.99                                                                  |

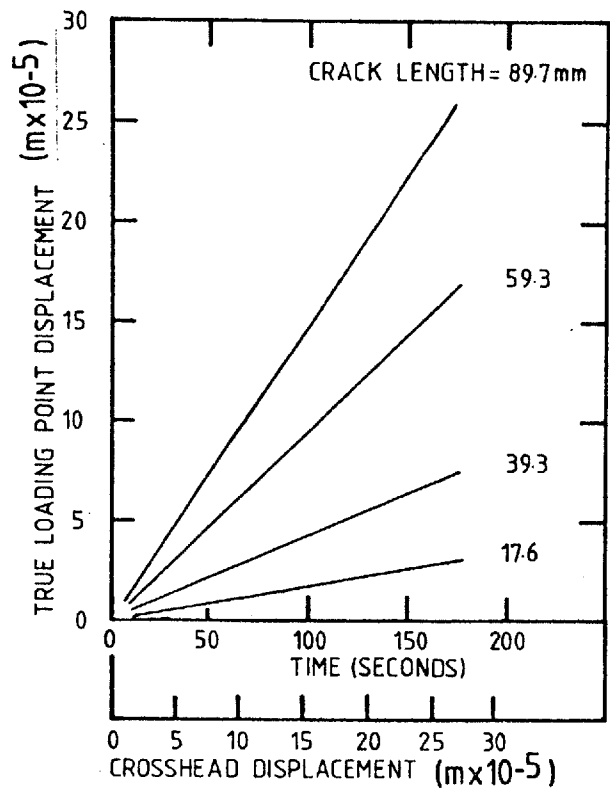


Figure 6.19a: Measurement of true loading point compliance  $C_{TLP}$  for artificial crack lengths (cross-head speed -  $1.02 \times 10^{-4} \text{ m min}^{-1}$ ).

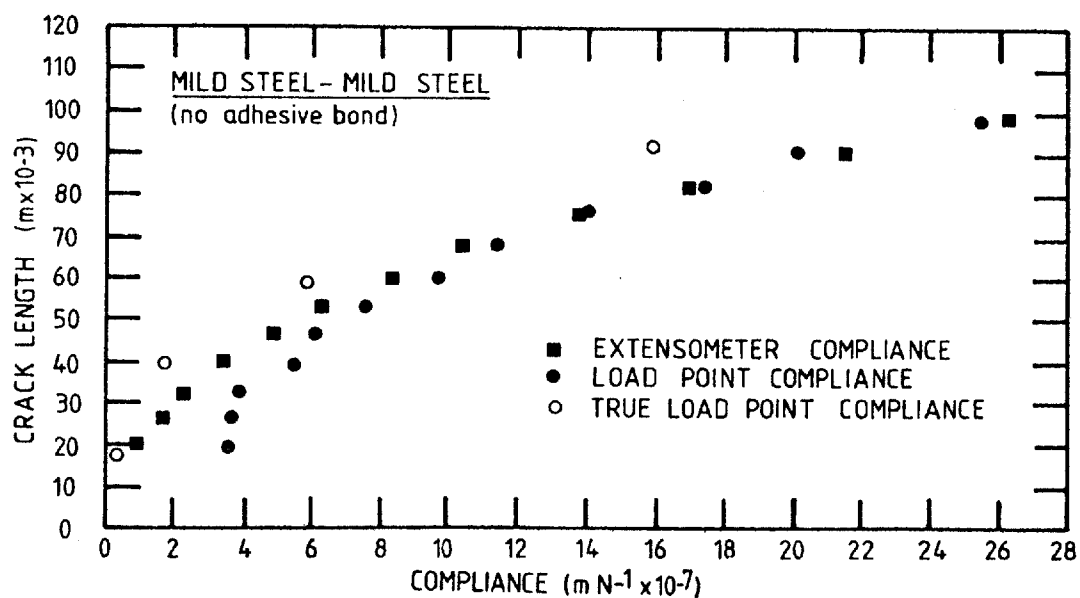


Figure 6.19b: Comparison of  $C_E$ ,  $C_{LP}$  and  $C_{TLP}$  for a mild steel (no adhesive joint) DCB specimen.

A dial gauge was placed between the moving and fixed cross-heads and verified that the cross-head displacement was  $1.02 \times 10^{-4} \text{ m min}^{-1}$  at forces up to  $1.8 \times 10^3 \text{ N}$ , and so it could not be argued that the low cross-head rate resulted from slipping of the friction clutch of the testing machine. On the other hand the displacement rate varied significantly when the dial gauge was positioned between the moving cross-head and various positions up to the fixed cross-head. Figure 6.20 shows the displacements recorded over time intervals of one minute for a relatively stiff mild steel tensile specimen with cross-section dimensions of  $14 \text{ mm} \times 5 \text{ mm}$  and a gauge length of  $100 \text{ mm}$ . Clearly there is a substantial contribution to the extensometer compliance from elastic deformation of the pin assembly (or grips).

#### 6.5.2.4 Discussion

The compliance calibration enabled the crack length to be determined indirectly during the progress of an experiment, but it is still important to analyse how the cantilever arms bend during a test so that the fracture toughness, as shown in section 6.5.3.1, can be calculated. The arms behave (figure 6.21) either:-

- (i) as rigid beams pivoting about the joined end;
- (ii) as cantilever beams which are built in at the crack-tip;
- (iii) as cantilever beams which rotate at some point beyond the crack-tip.,

and these different models will be discussed in turn. In particular model (iii) is examined in relation to the work of Mostovoy et al., (1967).

#### Rigid Arm Model

Figure 6.22 represents the displacement of one arm if it is assumed rigid and to pivot about the joined end. The displacements of the extensometer and at the load point are approximately equal to  $\Delta_E$  and  $\Delta_{TLP}$  for small rotations of the beam, as shown; and these displacements can be considered the same as those of  $\mu_E$  and  $\mu_{TLP}$  about the pivot point. Therefore the ratio of  $\mu_E/\mu_{TLP}$  is determined by the

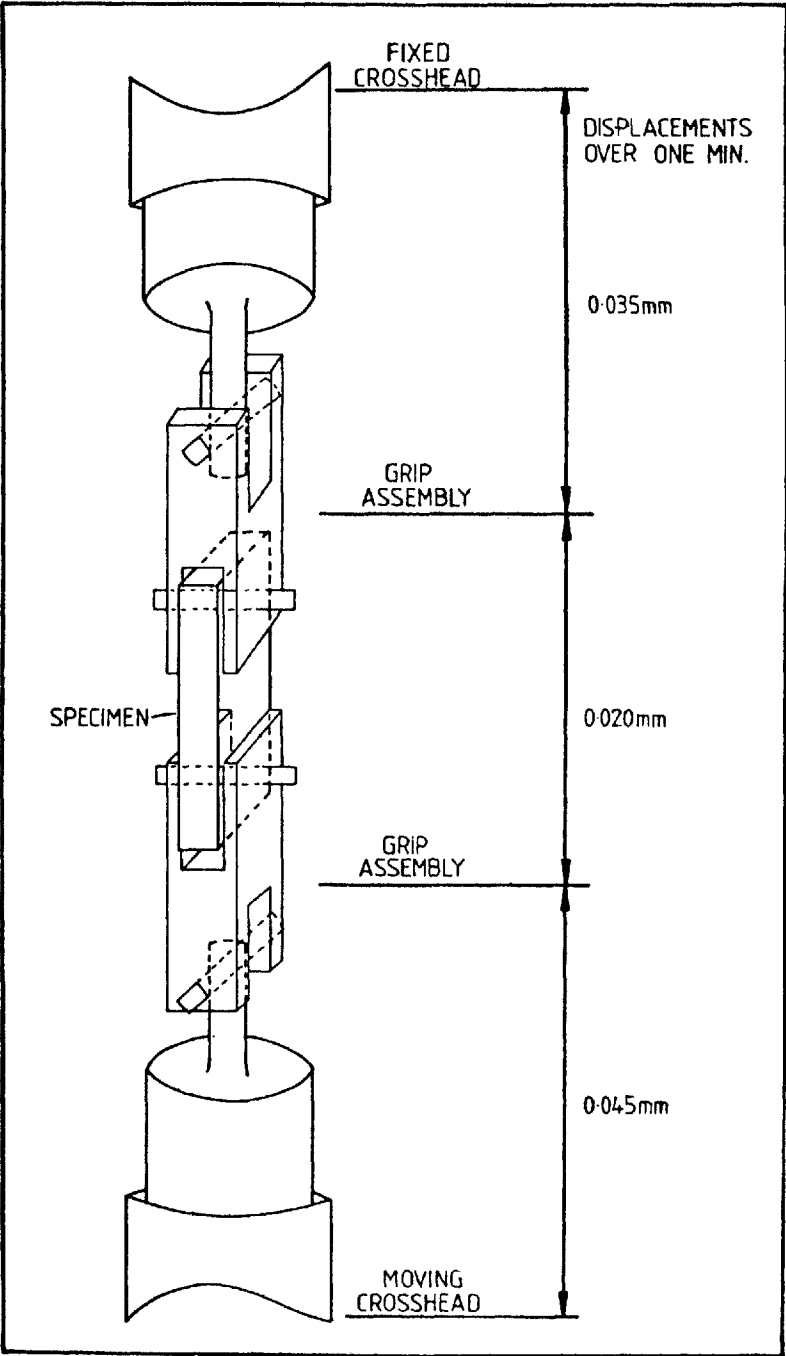


Figure 6.20: Relative displacements of various parts of the testing arrangement when measured after one minute.

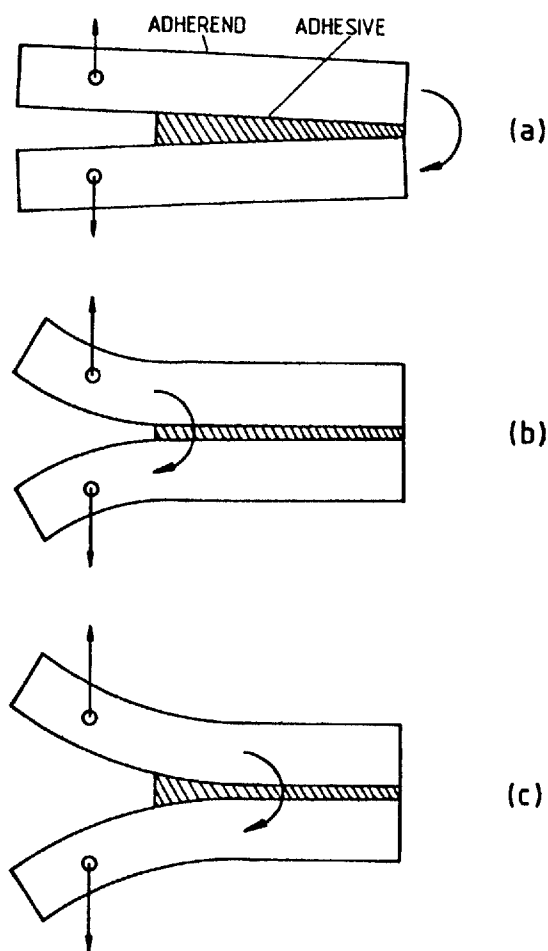


Figure 6.21: Bending modes of DCB specimen.  
 (a) rigid arms  
 (b) cantilever beams built in at the crack-tip  
 (c) rotation of cantilever beams at a point beyond crack-tip.

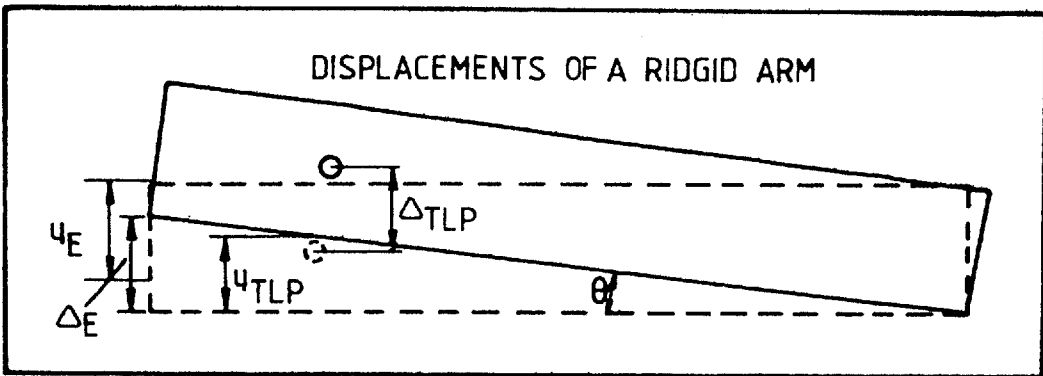


Figure 6.22: Displacement of a cantilever arm.

specimen geometry regardless of the crack length and in the case of this work is :-

$$\begin{aligned}\frac{\mu_E}{\mu_{TLP}} &= \frac{\text{total specimen length}}{\text{specimen length from the load point to the pivot end}} \\ &= \frac{156}{156-22} \quad \dots (6.30) \\ &= 1.16\end{aligned}$$

The compliance ratio,  $C_E/C_{TLP}$ , is thus the same as the displacement ratio, however the experimental values in Table 6.5 show that this value is not a constant, and thus the simple model given by equation 6.30 can be discounted.

Table 6.5:  $C_E/C_{TLP}$  Ratios

| Crack length<br>$\times 10^{-3} \text{ m}$ | $C_E/C_{TLP}$<br>Theory | $C_E/C_{TLP}$<br>Experimental |
|--------------------------------------------|-------------------------|-------------------------------|
| 17.6                                       | 2.25                    | 2.17                          |
| 39.3                                       | 1.56                    | 1.88                          |
| 59.3                                       | 1.39                    | 1.19                          |
| 89.7                                       | 1.25                    | 1.04                          |

#### Cantilever beams built in at the crack tip

The theoretical values in Table 6.5 refer to the model (Figure 6.21b) where the cantilever arms are considered to bend insignificantly (i.e. they are rigid) from the crack tip. The compliance ratio in this case is given by:-

$$\frac{C_E}{C_{TLP}} = \frac{22 \times 10^{-3} + \ell}{\ell} \quad \dots (6.31)$$

where  $\ell$  = crack length (m)



$$C = \frac{2}{3EI} ((\ell + \ell_o)^3 + h^2 \ell) \quad \dots (6.34a)$$

where additionally  $\ell_o$  = offset of  $0.6h$  due to beam rotation at the crack tip

$h^2 \ell$  = correction for shear with the assumption that Poisson's ratio is 0.33.

After inserting the constant terms (given in equation 6.33) for mild steel adherends :-

$$C = 7.937 \times 10^{-4} ((\ell + 1.2 \times 10^{-2})^3 + (4 \times 10^{-4} \times \ell)) \quad \dots (6.34b)$$

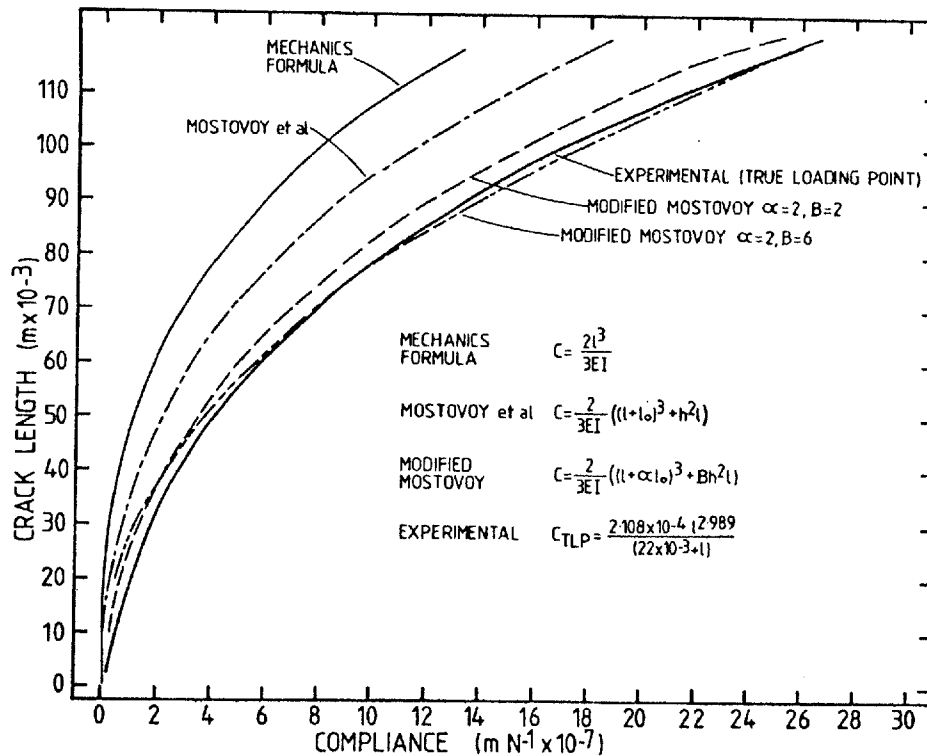


Figure 6.23: Experimental compliance - crack length functions compared to various theories.

The theory of Mostovoy et al., is a closer approximation to the experimental results of the present work; however the correction factors of equation 6.34a do not completely account for the cantilever arm deformation. Therefore the experimental data obtained in this study was fitted to a modification of Mostovoy's compliance equation which had the form of :-

$$C = \frac{2}{3EI} ((\ell + \alpha \ell_o)^3 + \beta h^2 \ell) \quad \dots (6.35)$$

where  $\alpha$  = empirical constant which implies bending beyond the crack tip

$\beta$  = empirical constant assuming displacement and shear at the crack tip.

Several sets of data for this compliance relation with  $\alpha = 2$  and  $\beta = 2$  or  $6$  are shown in Figure 6.23. It is seen that the theoretical compliance corresponds closely to the experimental results when  $\alpha$  and  $\beta$  are greater than 1. This indicates that the cantilever arms bend significantly beyond the crack tip and that the adhesive is deformed. Therefore it would be expected that the terms of  $\alpha$  and  $\beta$  could be related to the specimen dimensions and material properties of the adherends and adhesive, as it has been done in the work of Mostovoy et al, (1967), however this has not been attempted in the present study. The major result of the compliance measurements was that  $C_{TLP}$  was related to  $C_E$  via equation (6.32), and this was carried out by examining the deformation of the cantilever arms.

#### Grip compliance of the testing arrangement

A major anomaly raised in section 6.5.2.3 was related to the calculation of  $C_{LP}$ . For example it has already been discussed that errors in the  $C_{LP}$  calculation arose due to the assumption of a linear loading curve. However a more significant feature of these measurements concerns the shape of the curves in Figure 6.18 since the extrapolation to zero crack length resulted in a finite compliance. It will be shown that this compliance value can also be termed the "grip compliance" and eventuates from elastic deformation of the grip and pin assembly which is used to hold the specimen. Therefore the total compliance of a closed testing system can be expressed as:-

$$C_{TOT} = C_G + C_S \quad \dots (6.36a)$$

where  $C_{TOT}$  = total compliance ( $\text{mN}^{-1}$ )  
 $C_G$  = grip compliance ( $\text{mN}^{-1}$ )  
 $C_S$  = specimen compliance ( $\text{mN}^{-1}$ ).

In the case of this work the total compliance was measured between the fixed and moving cross-heads of the tensile testing machine and is equivalent to  $C_{LP}$ , whereas the specimen compliance was measured between the load points and is the same as  $C_{TLP}$ . Therefore equation (6.36a) can be modified to the nomenclature of this work to:-

$$C_{LP} = C_G + C_{TLP}$$

so that  $C_G = C_{LP} - C_{TLP} \quad \dots (6.36b)$

The grip compliance, for data which was presented in Figure 6.19a and Table 6.4, is shown for 4 crack lengths in Table 6.6.

Table 6.6: Grip compliance at 4 crack lengths

| Crack length<br>( $\times 10^{-3}$ m) | Grip Compliance<br>( $\times 10^{-7}$ $\text{mN}^{-1}$ ) |
|---------------------------------------|----------------------------------------------------------|
| 17.6                                  | 3.0                                                      |
| 39.3                                  | 3.4                                                      |
| 59.3                                  | 4.5                                                      |
| 89.7                                  | 3.9                                                      |

It should be pointed out that these compliance values are sensitive to errors in the displacement measurement which may arise due to back-lash of the main lead screws (approximately  $1.5 \times 10^{-5}$  m) of the tensile testing machine. Errors of this type have been avoided since  $C_{LP}$  and  $C_{TLP}$  were calculated after the back-lash was taken up. Also it is not clear from Figure 6.19b that  $C_{LP}$  and  $C_{TLP}$  differ at large crack lengths by an additional factor of  $C_G$ . The

relative contribution of  $C_G$  to the total compliance is significant up to crack lengths of 100 mm and ranges from  $3.0$  to  $4.5 \times 10^{-7} \text{ mN}^{-1}$ .

The  $C_{TLP}$  of an uncracked specimen will approach zero (but still have a small finite compliance) as can be established by inserting a zero crack length into the generalised formula 6.35. Therefore equation 6.36b was used to estimate  $C_G$  as  $2.75 \times 10^{-7} \text{ mN}^{-1}$  by extrapolating the  $C_{LP}$  - crack length curves (Figure 6.18a) to a zero crack length.

The grip compliance was used to measure the rigidity of the experimental arrangement via the expression:-

$$E b C_G \quad \dots (6.37a)$$

where  $E$  = Young's modulus of specimen arms (Pa)

$b$  = specimen arm width (m)

$C_G$  = grip compliance ( $\text{mN}^{-1}$ ).

For a mild steel specimen where :-

$$E = 210 \times 10^9 \text{ Pa}$$

$$b = 6 \times 10^{-3} \text{ m}$$

and

$$\begin{aligned} E b C_G &= 280 \text{ if } C_G = 2.75 \times 10^{-7} \text{ mN}^{-1} \\ E b C_G &= 470 \text{ if } C_G = 4.5 \times 10^{-7} \text{ mN}^{-1} \end{aligned} \quad \dots (6.37b)$$

It has been reported (Clausing, 1969) that a value for  $E b C_G$  of 600 is representative of a soft (load controlled) machine whereas a hard (displacement controlled) machine has a value of 1.5. In the case of the present experiments the conditions are soft and the geometric stability factor (gsf) determined from Figure 6.24, ranges from +5 to -5 for mild steel specimens. It has already been mentioned in section 6.4.1 that a specimen is more stable against cracking for the more negative gsf.

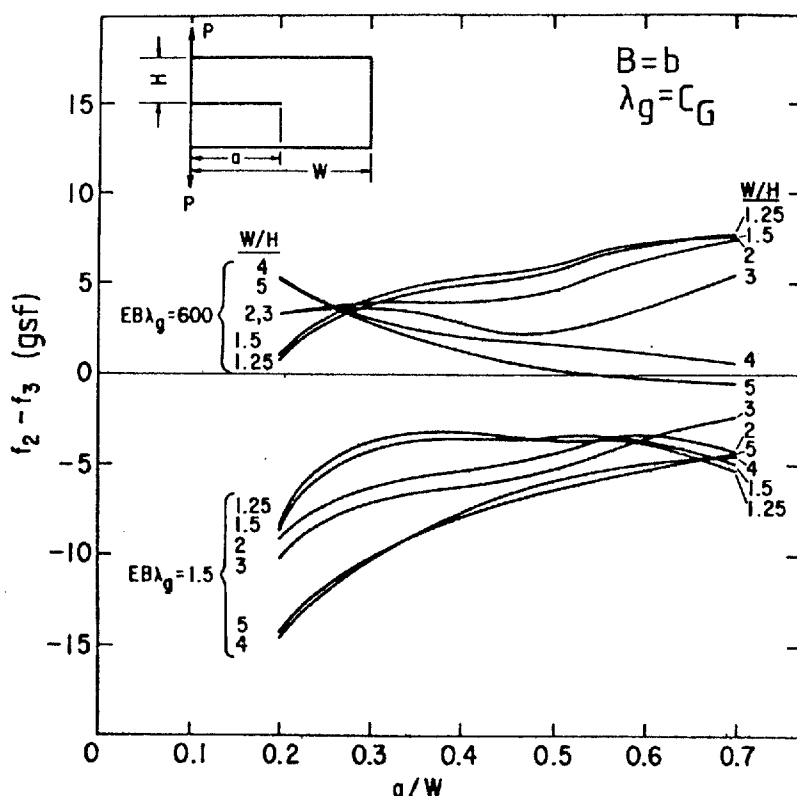


Figure 6.24: Geometric stability factors for parallel sided DCB (Clausing, 1969).

The  $C_{TLP}$  of the aluminium and aluminium-mild steel specimens was not established but in both cases (Figure 6.18b) the  $C_{LP}$  - crack length curves approached about  $3.5 \times 10^{-7} \text{ mN}^{-1}$  for a zero crack length. It is reasonable to assume that these specimens behave in a similar manner to the mild steel specimens and thus for the aluminium adherend specimen.

$$E b C_G = 149 \quad \dots (6.37c)$$

This indicates that the aluminium specimen resulted in a more rigid experimental arrangement compared to the mild steel sample and thus the gsf was lower.

Thus a major feature of the fracture toughness measurements which are described in section 6.5.3.2 was that soft machine testing conditions were used. This infers that the optimum experimental arrangement for stable crack growth was not available and this point is examined further in section 6.5.4.2.

### 6.5.3 Double Cantilever Beam Measurements

#### 6.5.3.1 Introduction

This section describes DCB tests that were carried out on coatings in order to determine their fracture toughness. It has already been shown that the true loading point compliance of the DCB geometry that was chosen to test coatings was related to the extensometer compliance by the relation:-

$$\frac{C_E}{C_{TLP}} = \frac{22 \times 10^{-3} + \ell}{\ell} \quad \dots (6.31)$$

Also an empirical equation was established to relate the extensometer compliance to the crack length:-

$$C_E = 2.108 \times 10^{-4} \ell^{1.989} \quad \dots (6.29)$$

Therefore it was found :-

$$C_{TLP} = \frac{2.108 \times 10^{-4} \ell^{2.989}}{(22 \times 10^{-3} + \ell)} \quad \dots (6.32)$$

The fracture toughness of the coating is determined by using equation 6.24 which has been expressed below in the nomenclature used in this thesis:

$$G = \frac{F^2}{2b} \frac{d C_{TLP}}{d \ell} \quad \dots (6.24)$$

The derivative term in equation 6.24 can be found as :-

$$\frac{d C_{TLP}}{d \ell} = \frac{6.3 \times 10^{-4} \ell^{1.989}}{(22 \times 10^{-3} + \ell)} - \frac{2.108 \times 10^{-4} \ell^{2.989}}{(22 \times 10^{-3} + \ell)^2} \quad \dots (6.38)$$

Thus the complete expression at the critical value for mode I cracking is :

$$G_{IC} = \frac{F_C^2}{(2b)} \left| \frac{6.3 \times 10^{-4} \ell^{1.989}}{(22 \times 10^{-3} + \ell)} - \frac{2.108 \times 10^{-4} \ell^{2.989}}{(22 \times 10^{-3} + \ell)^2} \right| \dots (6.39)$$

Therefore it is necessary to determine the crack length from  $C_E$  (via equation 6.29) and then use the critical force value to find the critical fracture toughness (critical strain energy release rate).

The above analysis was carried out for metal (mild steel and Ni-Al) ceramic ( $Al_2O_3$ - $TiO_2$ ) and composite layer (Ni-Al +  $Al_2O_3$ - $TiO_2$ ) plasma sprayed coatings. Also the fracture morphology of the coatings, in relation to the fracture toughness, is reported in this section.

#### 6.5.3.2 Experiments

Plasma sprayed coatings prepared according to the schedule of Table 4.3 were tested by the DCB method; these coatings are summarised in Table 6.7. Generally 5 samples were coated at the same time by traversing the torch (torch to substrate distance of 15 cm) across the specimen and working along the length of the specimen so that the deposit was laid down in a raster pattern onto the substrate. In this way it was expected that the coating properties would be typical of those prepared industrially. For example if the case of substrates being sprayed along their length is considered, then only the particles with the highest velocity and temperature at the center of the plasma jet, would form the coating. These particles would be expected to confer superior mechanical properties than a coating produced from particles with a complete range of temperatures and velocities (as indicated in Figure 2.8).

Table 6.7: Coatings used for DCB tests

- |     |                                                  |
|-----|--------------------------------------------------|
| (1) | Nickel - 4.5% Aluminium (Metco 450)              |
| (2) | Mild steel (Metco 91)                            |
| (3) | Alumina - 2.5% Titania (Metco 101)               |
| (4) | Nickel - 4.5% Aluminium + Alumina - 2.5% Titania |

The DT, compliance and DCB specimens were prepared in exactly the same manner (section 6.4.2). There were slight variations in the specimen width (about 5 mm for the DT specimens and 6 mm for both the compliance and DCB specimens) since the alignment of the sample in the mould when forming the adhesive joint was more precise in the latter tests. Therefore it was not necessary to extensively machine the specimens in order to make the 150 mm x 40 mm surfaces flat. Grooving of the specimens (Figure 6.25)

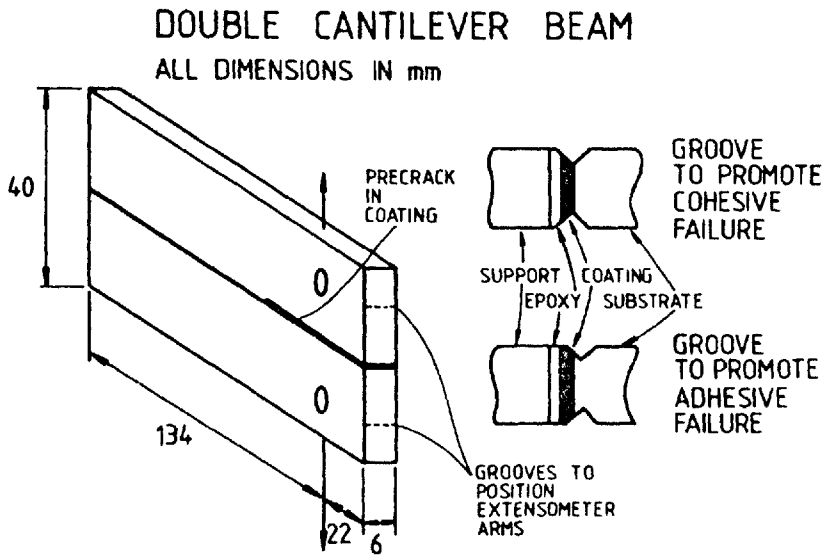


Figure 6.25: DCB specimens used for adhesion measurements. Inset shows the grooving procedure to promote either adhesive or cohesive failure.

by grinding in the vicinity of the interface was used to promote either adhesive or cohesive failure. It has already been established that grooving does not significantly affect the compliance ( $C_E$ ), however the reduced width of the coating must be used in equation 6.39 to find the fracture toughness.

Loading holes (6.4 mm diameter) were placed centrally in each cantilever arm and 22 mm from the free end of the beam. For the DCB specimen the pre-crack was a sawcut (0.2 mm thick) which extended about 20 mm from the loading axis. In this case the first extension of the pre-crack results in a sharp crack which can then be used in following measurements. It should be kept in mind though that the

nature of the pre-crack tip radius may not be too significant because,

- (i) natural micro-cracks already exist within the coating or,
- (ii) the crack tip radius may be controlled by the presence of porosity.

The specimens were tested in tension (Instron universal testing machine) at a cross-head displacement rate of  $1.02 \times 10^{-4} \text{ m min}^{-1}$ . The relative displacement of the arms was measured with a 25.4 mm gauge length, 0 to 10% extensometer. In some experiments the data acquisition system (section 6.5.2.2) was used to continuously monitor and periodically record (at 3 to 10 second intervals) the force and displacement; these measurements were used to calculate  $C_{TLP}$ .

#### 6.5.3.3 Results of Fracture Toughness Tests

The results of the DCB tests are summarised in Table 6.8 and Figure 6.26.

The load-displacement curves (Figure 6.27) show the onset of cracking when the initial linear region of the trace levels out. When the cross-head of the testing machine is stopped at this point the crack grows - as is evident by the compliance change of the specimens. This compliance change can be found in a number of ways which are illustrated in the inset diagram of Figure 6.27. The unloading curve (no. 3) was used to find the crack length for the next test and in this manner any anomalies associated with the initial loading of the specimen (such as misalignment of the grips) could be accounted for. Once the crack length and load is known equation 6.39 can be applied to find  $G_{IC}$ .

The above procedure can then be carried out again for the new crack length and it was found that generally about 5 to 8 measurements for metal coatings and about 2 to 4 measurements for ceramic coatings were obtained from each specimen.

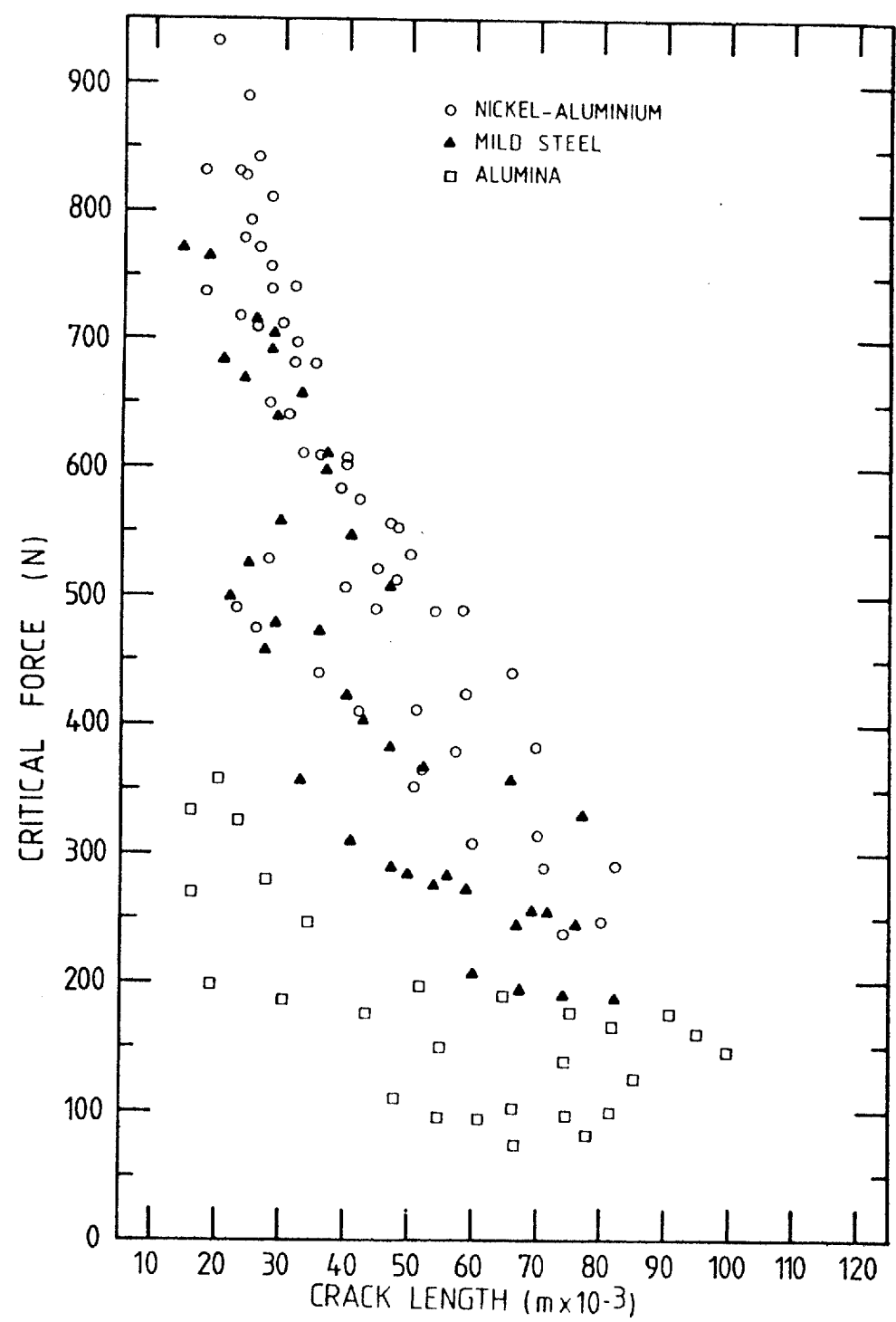


Figure 6.26: Critical force measurements for various coatings.

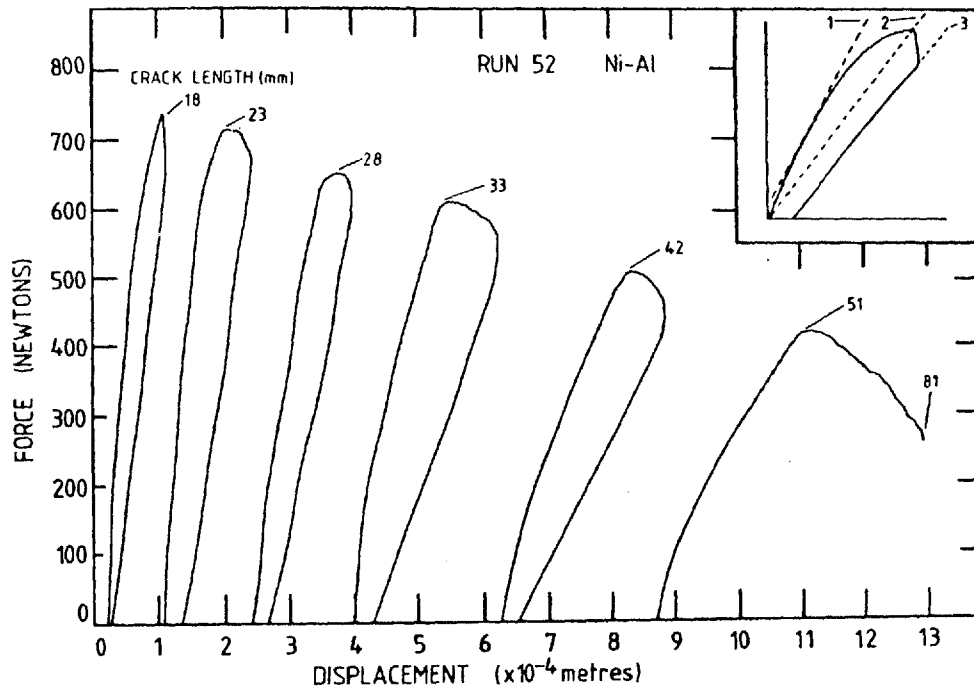


Figure 6.27: Force-displacement curves for a Ni-Al coating tested by the DCB method. Inset illustrates the various methods for determining the extensometer compliance.

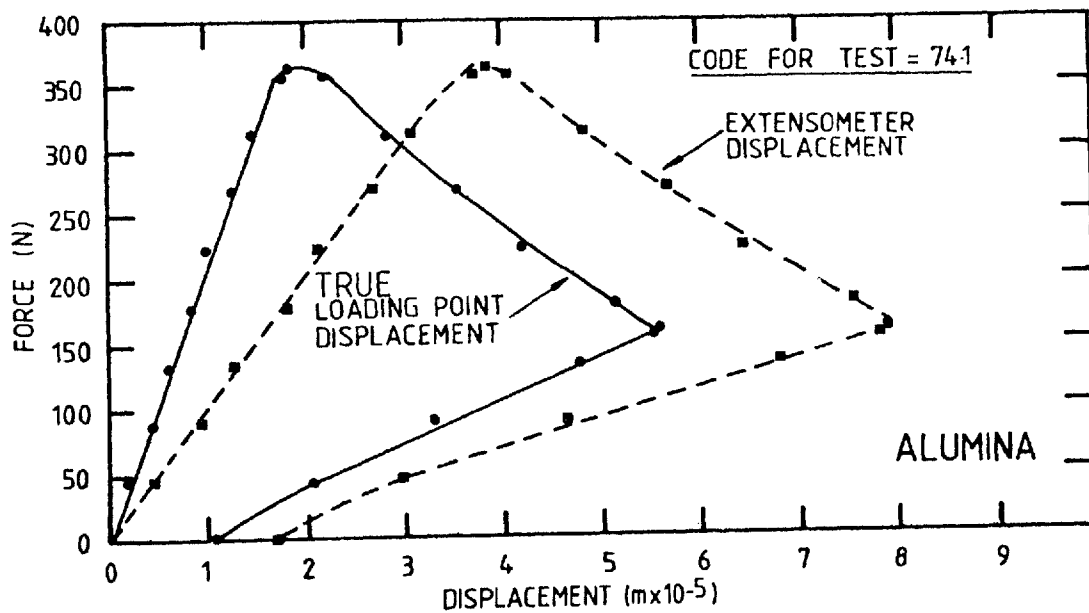


Figure 6.28: Measured extensometer displacement and calculated true loading point displacement for a  $\text{Al}_2\text{O}_3\text{-TiO}_2$  coating.

Table 6.8: Results of DCB Tests

## Ni-Al Coatings

| Specimen Designation | Compliance<br>( $\text{mN}^{-1} \times 10^{-7}$ ) | Crack Length<br>(mm) | Critical Force (N) | $G_{IC}$<br>( $\text{Jm}^{-2}$ ) | Specimen Designation | Compliance<br>( $\text{mN}^{-1} \times 10^{-7}$ ) | Crack Length<br>(mm) | Critical Force (N) | $G_{IC}$<br>( $\text{Jm}^{-2}$ ) |
|----------------------|---------------------------------------------------|----------------------|--------------------|----------------------------------|----------------------|---------------------------------------------------|----------------------|--------------------|----------------------------------|
| 51                   | 1.285                                             | 20                   | 499                | 109                              | 77                   | 4.774                                             | 47                   | 557                | 416                              |
|                      | 1.695                                             | 28                   | 468                | 152                              |                      | 5.424                                             | 50                   | 535                | 414                              |
|                      | 11.843                                            | 74                   | 241                | 133                              |                      | 6.336                                             | 54                   | 490                | 381                              |
| 52                   | 1.023                                             | 18                   | 739                | 206                              | 78                   | 9.415                                             | 66                   | 441                | 390                              |
|                      | 1.162                                             | 23                   | 722                | 278                              |                      | 1.027                                             | 17.5                 | 833                | 252                              |
|                      | 1.726                                             | 28                   | 650                | 294                              |                      | 1.229                                             | 24                   | 780                | 344                              |
| 76                   | 2.376                                             | 33                   | 610                | 321                              | LD5                  | 1.520                                             | 26                   | 708                | 316                              |
|                      | 3.877                                             | 42                   | 508                | 302                              |                      | 2.044                                             | 31                   | 641                | 327                              |
|                      | 5.609                                             | 51                   | 423                | 265                              |                      | 4.435                                             | 45                   | 521                | 346                              |
|                      | 1.267                                             | 23                   | 833                | 370                              |                      | 5.083                                             | 48                   | 512                | 361                              |
|                      | 1.483                                             | 26                   | 771                | 375                              |                      | 7.668                                             | 59                   | 423                | 315                              |
| 77                   | 1.717                                             | 28                   | 739                | 380                              | LD7                  | 1.380                                             | 25                   | 793                | 376                              |
|                      | 2.168                                             | 32                   | 682                | 386                              |                      | 1.685                                             | 28                   | 757                | 399                              |
|                      | 2.896                                             | 36                   | 610                | 359                              |                      | 2.214                                             | 32                   | 699                | 405                              |
|                      | 4.802                                             | 45                   | 490                | 306                              |                      | 3.492                                             | 40                   | 606                | 404                              |
|                      | 6.985                                             | 57                   | 383                | 248                              |                      | 4.987                                             | 48                   | 552                | 420                              |
|                      | 10.527                                            | 70                   | 327                | 229                              |                      | 7.267                                             | 58                   | 477                | 392                              |
|                      | 14.597                                            | 82                   | 290                | 216                              |                      | 10.606                                            | 70                   | 383                | 315                              |
|                      | 1.259                                             | 19.5                 | 935                | 370                              |                      | 1.939                                             | 28                   | 530                | 196                              |
|                      | 1.300                                             | 24                   | 891                | 449                              |                      | 2.900                                             | 36                   | 441                | 188                              |
|                      | 1.533                                             | 26                   | 846                | 451                              |                      | 3.801                                             | 42                   | 410                | 196                              |
| LD13                 | 1.742                                             | 28                   | 824                | 472                              | LD13                 | 5.702                                             | 51                   | 352                | 183                              |
|                      | 2.187                                             | 32                   | 744                | 459                              |                      | 7.920                                             | 60                   | 312                | 175                              |
|                      | 3.140                                             | 35                   | 682                | 433                              |                      | 1.274                                             | 24                   | 829                | 388                              |
|                      | 3.576                                             | 40                   | 601                | 398                              |                      | 1.990                                             | 30                   | 713                | 387                              |
|                      | 3.825                                             | 42                   | 579                | 392                              |                      | 3.290                                             | 39                   | 579                | 358                              |
|                      |                                                   |                      |                    |                                  |                      | 5.987                                             | 52                   | 365                | 202                              |
|                      |                                                   |                      |                    |                                  |                      | 11.048                                            | 71                   | 290                | 183                              |
|                      |                                                   |                      |                    |                                  |                      | 13.898                                            | 80                   | 249                | 155                              |

Table 6.8 (continued) Mild Steel Coatings

| Specimen Designation | Compliance<br>( $\text{mN}^{-1} \times 10^{-7}$ ) | Crack Length<br>(mm) | Critical Force (N) | $G_{IC}$<br>( $\text{Jm}^{-2}$ ) | Specimen Designation | Compliance<br>( $\text{mN}^{-1} \times 10^{-7}$ ) | Crack Length<br>(mm) | Critical Force (N) | $G_{IC}$<br>( $\text{Jm}^{-2}$ ) |
|----------------------|---------------------------------------------------|----------------------|--------------------|----------------------------------|----------------------|---------------------------------------------------|----------------------|--------------------|----------------------------------|
| 55                   | 0.689                                             | 14                   | 771                | 155                              | LD12                 | 1.515                                             | 26                   | 713                | 320                              |
|                      | 0.900                                             | 18                   | 766                | 222                              |                      | 1.738                                             | 28                   | 699                | 340                              |
|                      | 1.292                                             | 24                   | 668                | 252                              |                      | 2.348                                             | 33                   | 659                | 375                              |
|                      | 1.996                                             | 30                   | 557                | 236                              |                      | 3.005                                             | 37                   | 610                | 372                              |
|                      | 2.907                                             | 36                   | 472                | 215                              |                      | 3.629                                             | 41                   | 548                | 341                              |
|                      | 5.524                                             | 50                   | 285                | 117                              |                      |                                                   |                      |                    |                                  |
| LD1                  | 6.264                                             | 54                   | 276                | 121                              | LD14                 | 1.544                                             | 27                   | 459                | 140                              |
|                      | 7.547                                             | 59                   | 274                | 132                              |                      | 2.348                                             | 33                   | 356                | 110                              |
|                      | 9.831                                             | 67                   | 245                | 123                              |                      | 3.580                                             | 41                   | 307                | 107                              |
|                      | 14.445                                            | 82                   | 189                | 92                               |                      | 4.802                                             | 47                   | 290                | 113                              |
|                      |                                                   |                      |                    |                                  |                      | 6.842                                             | 56                   | 285                | 135                              |
|                      |                                                   |                      |                    |                                  |                      | 11.721                                            | 74                   | 192                | 84                               |
| LD6                  | 1.054                                             | 22                   | 499                | 125                              |                      |                                                   |                      |                    |                                  |
|                      | 1.808                                             | 29                   | 477                | 166                              |                      |                                                   |                      |                    |                                  |
|                      | 3.421                                             | 40                   | 423                | 197                              |                      |                                                   |                      |                    |                                  |
|                      | 11.104                                            | 72                   | 254                | 143                              |                      |                                                   |                      |                    |                                  |
|                      |                                                   |                      |                    |                                  |                      |                                                   |                      |                    |                                  |
|                      |                                                   |                      |                    |                                  |                      |                                                   |                      |                    |                                  |
| LD9                  | 0.970                                             | 21                   | 686                | 221                              |                      |                                                   |                      |                    |                                  |
|                      | 1.843                                             | 29                   | 637                | 296                              |                      |                                                   |                      |                    |                                  |
|                      | 3.974                                             | 43                   | 401                | 193                              |                      |                                                   |                      |                    |                                  |
|                      | 4.887                                             | 47                   | 383                | 197                              |                      |                                                   |                      |                    |                                  |
|                      | 5.940                                             | 52                   | 365                | 202                              |                      |                                                   |                      |                    |                                  |
|                      | 10.264                                            | 69                   | 256                | 138                              |                      |                                                   |                      |                    |                                  |
| LD11                 | 12.540                                            | 76                   | 245                | 141                              |                      |                                                   |                      |                    |                                  |
|                      |                                                   |                      |                    |                                  |                      |                                                   |                      |                    |                                  |
|                      | 1.336                                             | 25                   | 526                | 165                              |                      |                                                   |                      |                    |                                  |
|                      | 7.840                                             | 60                   | 209                | 79                               |                      |                                                   |                      |                    |                                  |
|                      | 9.693                                             | 67                   | 196                | 78                               |                      |                                                   |                      |                    |                                  |
|                      |                                                   |                      |                    |                                  |                      |                                                   |                      |                    |                                  |
| LD11                 | 1.697                                             | 28                   | 690                | 332                              |                      |                                                   |                      |                    |                                  |
|                      | 3.022                                             | 37                   | 597                | 356                              |                      |                                                   |                      |                    |                                  |
|                      | 4.904                                             | 47                   | 508                | 346                              |                      |                                                   |                      |                    |                                  |
|                      | 9.503                                             | 66                   | 356                | 255                              |                      |                                                   |                      |                    |                                  |
|                      | 12.905                                            | 77                   | 330                | 260                              |                      |                                                   |                      |                    |                                  |
|                      |                                                   |                      |                    |                                  |                      |                                                   |                      |                    |                                  |

Alumina Coatings

Table 6.8 (continued)

| Specimen Designation | Compliance<br>( $\text{mN}^{-1} \times 10^{-7}$ )            | Crack Length<br>(mm)                   | Critical Force (N)                            | $G_{IC}$<br>( $\text{Jm}^{-2}$ )       | Specimen Designation | Compliance<br>( $\text{mN}^{-1} \times 10^{-7}$ ) | Crack Length<br>(mm)       | Critical Force (N)              | $G_{IC}$<br>( $\text{Jm}^{-2}$ ) |
|----------------------|--------------------------------------------------------------|----------------------------------------|-----------------------------------------------|----------------------------------------|----------------------|---------------------------------------------------|----------------------------|---------------------------------|----------------------------------|
| 50                   | 1.180<br>1.983<br>5.069<br>9.863<br>13.034                   | 19<br>30<br>48<br>67<br>78             | 200<br>189<br>109<br>74<br>79                 | 16<br>27<br>16<br>11<br>15             | 74                   | 1.014<br>5.903<br>9.239<br>12.214<br>14.214       | 20<br>52<br>65<br>75<br>82 | 360<br>200<br>191<br>176<br>169 | 57<br>61<br>72<br>72<br>73       |
| 53                   | 0.974<br>1.252<br>1.711<br>2.486<br>4.073<br>6.517<br>11.931 | 16<br>23<br>28<br>34<br>43<br>55<br>74 | 334<br>325<br>281<br>247<br>178<br>149<br>143 | 35<br>56<br>55<br>55<br>38<br>36<br>47 | LD8                  | 18.175                                            | 91<br>100                  | 178<br>147                      | 92<br>68                         |
| 57                   | 20.528<br>22.808                                             | 97<br>103                              | 56<br>59                                      | 10<br>12                               |                      |                                                   |                            |                                 |                                  |
| 72                   | 0.695<br>6.676<br>8.050<br>9.503<br>11.918<br>14.602         | 16<br>55<br>61<br>66<br>75<br>82       | 272<br>98<br>98<br>105<br>99<br>100           | 24<br>16<br>18<br>22<br>23<br>26       |                      |                                                   |                            |                                 |                                  |

The true loading point displacement (Figure 6.28) was established from the extensometer displacement via equation 6.31 since the force is constant. The data points in Figure 6.28 are not related to measurements of equal time intervals but were values from the original Instron loading trace. A few general features of the DCB specimen behaviour for metal and ceramic coatings can also be seen by comparing Figures 6.27 and 6.28 respectively. For equivalent crack lengths the metal coatings exhibited:-

- (i) a higher critical force,
- (ii) a greater extensometer displacement, and
- (iii) less susceptibility for cracks to jump large distances (as indicated by the change in  $C_E$ ).

Both types of coatings exhibited the common feature that the force-displacement curve did not return to the origin on unloading and this behaviour is referred to as the "off-set" displacement. All of these factors are discussed further in section 6.5.4.

The experimental arrangement also had the facility that force-displacement data could be recorded with respect to time. Thus the time lapse between the onset of cracking and the end of crack growth was used, with the crack lengths obtained from the compliance measurements for loading and unloading (curves 1 and 3 respectively for the inset of Figure 6.27), to find the average crack speed. Table 6.9 shows a series of these calculations for a mild steel coating where the average crack speed ranges from  $0.1$  to  $1 \text{ mm sec}^{-1}$ . It was expected that the instantaneous crack velocity was much higher but tests did not confirm this. For example it was thought that crack growth could be monitored by assuming that the force-displacement trace returned to the origin if the specimen was instantaneously unloaded at some point after the onset of cracking. However this treatment does not account for the off-set displacement which may alter  $C_E$  significantly (and thus change the crack length determination). Thus at the relatively low crack speeds of these experiments it is not necessary to include a kinetic energy term in the calculation of  $G_{IC}$ . The dynamic behaviour of a crack only becomes significant at crack speeds in excess of  $1 \text{ m sec}^{-1}$  (Lawn and Wilshaw, 1975; pp. 91-108).

Table 6.9: Crack velocities for a mild steel coating

| Experimental Code | Crack Propagation distance (mm) | Crack Velocity ( $\times 10^{-4}$ m sec $^{-1}$ ) |
|-------------------|---------------------------------|---------------------------------------------------|
| 6.0               | 21-29                           | 4.7                                               |
| 6.1               | 29-43                           | 6.3                                               |
| 6.2               | 43-47                           | 10.0                                              |
| 6.3               | 47-52                           | 1.0                                               |
| 6.4               | 52-69                           | 7.3                                               |
| 6.5               | 69-76                           | 5.8                                               |

Table 6.10: Determination of Fracture Toughness from the area enclosed by the Force-Displacement Curve.

| Ni-Al coatings       |                 |                                  |                             |                                     |                                            |
|----------------------|-----------------|----------------------------------|-----------------------------|-------------------------------------|--------------------------------------------|
| Specimen designation | Crack jump (mm) | Area ( $\times 10^{-3}$ m $^2$ ) | Area $G_{IC}$ (mN $^{-1}$ ) | Compliance $G_{IC}$ (mN $^{-1}$ ) * | Off-set displacement ( $\times 10^{-6}$ m) |
| 52.1                 | 18-23           | 9.19                             | 153                         | 206                                 | 10.4                                       |
| .2                   | 23-28           | 21.30                            | 355                         | 278                                 | 16.6                                       |
| .3                   | 28-33           | 18.90                            | 315                         | 294                                 | 12.8                                       |
| .4                   | 33-42           | 31.20                            | 288                         | 321                                 | 19.8                                       |
| .5                   | 42-51           | 29.75                            | 275                         | 302                                 | 16.0                                       |
| 76.2                 | 23-26           | 15.83                            | 440                         | 370                                 | 10.6                                       |
| .3                   | 26-28           | 12.25                            | 510                         | 375                                 | 6.0                                        |
| .4                   | 28-32           | 17.44                            | 363                         | 380                                 | 9.0                                        |
| .5                   | 32-36           | 23.91                            | 498                         | 386                                 | 10.9                                       |
| .6                   | 36-45           | 41.21                            | 382                         | 359                                 | 24.9                                       |
| .7                   | 45-57           | 44.70                            | 258                         | 306                                 | 18.7                                       |
| .8                   | 57-70           | 19.19                            | 123                         | 248                                 | 2.9                                        |
| .9                   | 70-82           | 23.49                            | 163                         | 229                                 | 9.4                                        |
| 77.1                 | 19.5-24         | 1.59                             | 295                         | 370                                 | 12.7                                       |
| .2                   | 24-26           | 12.73                            | 530                         | 449                                 | 5.6                                        |
| .3                   | 26-32           | 26.26                            | 365                         | 451                                 | 14.4                                       |
| .4                   | 32-40           | 39.74                            | 414                         | 459                                 | 21.0                                       |
| .5                   | 40-54           | 46.31                            | 276                         | 398                                 | 23.0                                       |
| .6                   | 54-66           | 37.37                            | 259                         | 381                                 | 12.8                                       |

continued

Table 6.10 (continued)

| <u>Ni-Al Coatings (continued)</u>                                |                 |                                       |                                    |                                        |                                                     |
|------------------------------------------------------------------|-----------------|---------------------------------------|------------------------------------|----------------------------------------|-----------------------------------------------------|
| Specimen designation                                             | Crack jump (mm) | Area ( $\times 10^{-3} \text{ m}^2$ ) | Area ( $G_{IC} (\text{mN}^{-1})$ ) | Compliance $G_{IC} (\text{mN}^{-1})^*$ | Off-set displacement ( $\times 10^{-6} \text{ m}$ ) |
| 78.1                                                             | 17.5-24         | 11.57                                 | 148                                | 252                                    | 11.4                                                |
| .2                                                               | 24-26           | 13.36                                 | 557                                | 344                                    | 7.3                                                 |
| .3                                                               | 26-31           | 16.41                                 | 274                                | 316                                    | 9.1                                                 |
| .4                                                               | 31-45           | 27.30                                 | 163                                | 327                                    | 16.0                                                |
| .5                                                               | 45-48           | 10.05                                 | 279                                | 346                                    | 3.3                                                 |
| .6                                                               | 48-59           | 25.50                                 | 193                                | 361                                    | 11.3                                                |
| .7                                                               | 59-95           | 71.00                                 | 164                                | 315                                    | 33.6                                                |
| <u>Mild Steel Coatings</u>                                       |                 |                                       |                                    |                                        |                                                     |
| 55.1                                                             | 14-18           | 5.57                                  | 116                                | 155                                    | 3.4                                                 |
| .2                                                               | 18-24           | 9.39                                  | 130                                | 222                                    | 6.0                                                 |
| .3                                                               | 24-30           | 14.97                                 | 208                                | 252                                    | 8.9                                                 |
| .4                                                               | 30-36           | 13.32                                 | 185                                | 236                                    | 7.6                                                 |
| .5                                                               | 36-50           | 21.33                                 | 127                                | 215                                    | 19.5                                                |
| .6                                                               | 50-82           | 30.86                                 | 80                                 | 117                                    | 33.2                                                |
| 6.0                                                              | 21-29           | 5.50                                  | 57                                 | 221                                    | 12.1                                                |
| .1                                                               | 29-43           | 20.49                                 | 122                                | 296                                    | 18.8                                                |
| .2                                                               | 43-47           | 6.86                                  | 143                                | 193                                    | 0.8                                                 |
| .3                                                               | 47-52           | 7.92                                  | 132                                | 197                                    | 1.1                                                 |
| .4                                                               | 52-69           | 16.13                                 | 79                                 | 202                                    | 9.5                                                 |
| .5                                                               | 69-76           | 5.90                                  | 70                                 | 138                                    | 1.6                                                 |
| <u>Alumina Coatings</u>                                          |                 |                                       |                                    |                                        |                                                     |
| 53.1                                                             | 16-23           | 2.01                                  | 24                                 | 35                                     | 6.9                                                 |
| .2                                                               | 23-28           | 3.78                                  | 63                                 | 56                                     | 6.4                                                 |
| .3                                                               | 28-34           | 3.18                                  | 44                                 | 55                                     | 4.5                                                 |
| .4                                                               | 34-43           | 5.96                                  | 55                                 | 55                                     | 11.4                                                |
| .5                                                               | 43-55           | 3.83                                  | 27                                 | 38                                     | 6.7                                                 |
| .6                                                               | 55-74           | 12.90                                 | 57                                 | 36                                     | 30.4                                                |
| 74.1                                                             | 20-52           | 6.90                                  | 18                                 | 57                                     | 11.8                                                |
| .3                                                               | 52-65           | 4.71                                  | 30                                 | 61                                     | 3.6                                                 |
| .4                                                               | 65-75           | 4.25                                  | 35                                 | 72                                     | 3.3                                                 |
| .5                                                               | 75-82           | 4.11                                  | 49                                 | 72                                     | 2.2                                                 |
| * From Table 6.8 and calculated via the compliance measurements. |                 |                                       |                                    |                                        |                                                     |

For some specimens the area bounded by the true loading point displacement versus force curve was calculated using an iterative quadrature technique and the strain energy release rate determined by using the formula :-

$$G_{IC} = \frac{A_1}{\text{crack surface area}} \quad \dots (6.26)$$

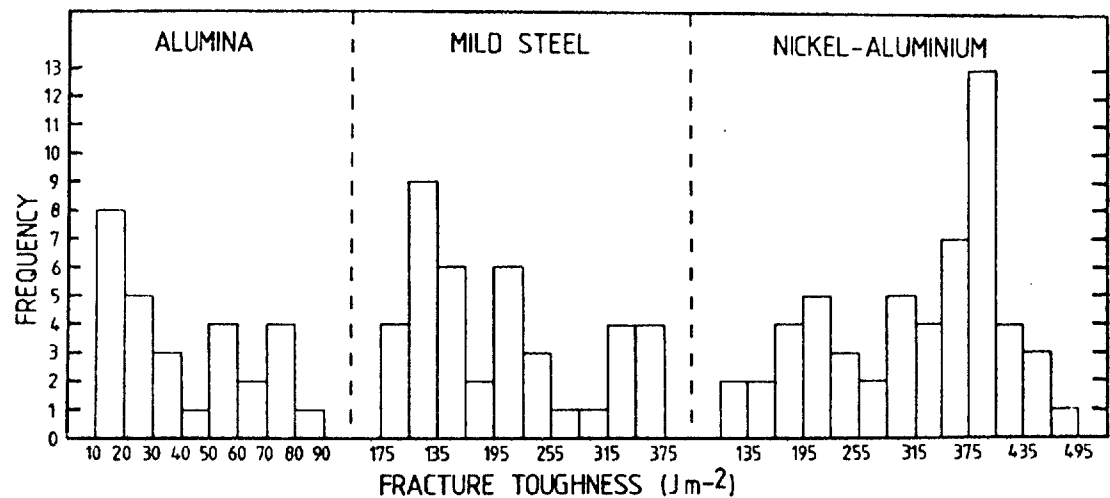
where  $A_1$  = the area enclosed by the true loading point displacement versus force curve (N-m or J).

$$\text{crack surface area} = (\ell_F - \ell_I) \times b \times 2$$

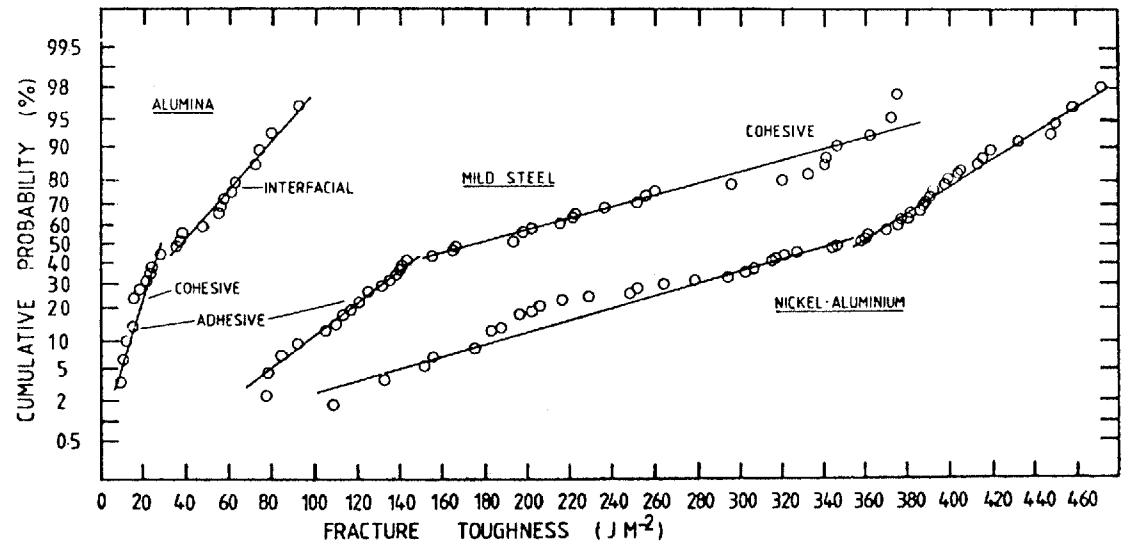
where  $\ell_F$  = final crack length (m)  
 $\ell_I$  = initial crack length (m)  
 $b$  = width of crack (m).

The factor of "2" in the above expression arises since two new fracture surfaces are created on cracking. Table 6.10 shows the area and fracture toughness calculations as well as the off-set displacements for some selected tests. Generally the calculation of  $G_{IC}$  from the area (equation 6.26) was less than the compliance  $G_{IC}$  (equation 6.39). The  $G_{IC}$  values calculated from the direct measurement of compliance are considered more reliable than those established from the area under the curve since, in the former case, errors due to the true loading point displacement calculation and the off-set displacement are minimal. The following sections therefore refer mostly to the compliance  $G_{IC}$  unless specified otherwise.

The distribution of the  $G_{IC}$  values for similar coatings (Table 6.8) was large so the individual results were ranked and histograms and probability plots constructed to observe trends (Figure 6.29). The histogram chart of each coating revealed distinct bimodal distributions which were also skewed. The probability plots show that each set of data does not fit a normal distribution and that the separate regions can be related (Table 6.11) to the fracture appearance that is described in the following section.



(a)



(b)

Figure 6.29: DCB results for alumina, nickel-aluminium and mild steel coatings.  
(a) Histograms  
(b) Probability plots.

Table 6.11:  $G_{IC}$  results of coatings (on mild steel substrates).

| Coating                              | Failure Type                    | $G_{IC}$ ( $Jm^{-2}$ ) |      |                    |
|--------------------------------------|---------------------------------|------------------------|------|--------------------|
|                                      |                                 | Range                  | Mean | Standard Deviation |
| Metco 91<br>(Mild steel)             | Adhesive                        | 78-143                 | 116  | 21                 |
|                                      | Cohesive                        | 155-375                | 261  | 71                 |
| Metco 450<br>(Ni-Al)                 | Cohesive                        | 109-472                | 319  | 95                 |
| Metco 101<br>( $Al_2O_3$ - $TiO_2$ ) | Cohesive                        | 16-27                  | 21   | 5                  |
|                                      | Adhesive (mild steel substrate) | 10-15                  | 12   | 2                  |
|                                      | Adhesive (Ni-Al sub-coat)       | 35-95                  | 58   | 16                 |

#### 6.5.3.4 Results of Fractography

The Ni-Al coatings failed in a cohesive mode and no distinction was observed in the fracture morphology which would explain the bimodal distribution of the fracture toughness results. Two types of failure were evident in the low fracture toughness range of the alumina<sup>\*</sup> coatings and these corresponded to respectively adhesive and cohesive failures at low and high fracture toughness values. Failure at the interface between the bond and ceramic coatings occurred with a higher fracture toughness than failure within the ceramic or at the substrate surface. The fracture toughness properties of the mild steel coatings were also bimodal with adhesive failure dominating at low values and cohesive failure at high values. However a cursory examination of the fracture surfaces did not reveal any marked differences between the two fracture modes represented by high and low fracture toughness. The fracture surfaces appeared to be predominantly

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\* The term "alumina" is used to describe the " $Al_2O_3$ - $TiO_2$ " powder used in this study and is also known under the trade name of "Metco 101".

adhesive in nature but a more thorough examination showed a greater degree of failure within the coating for the high fracture toughness values.

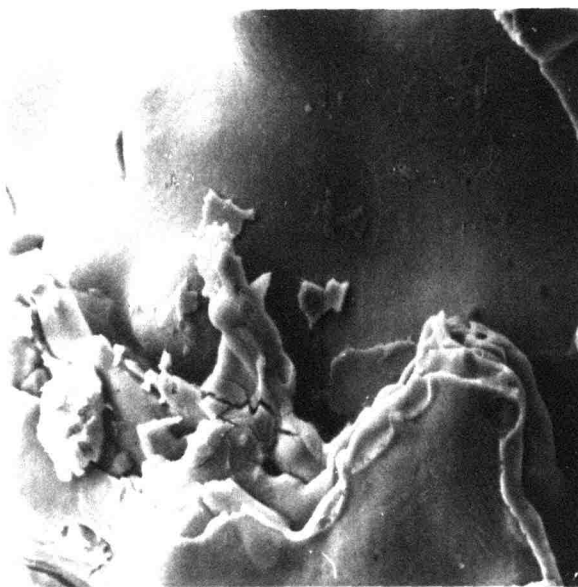
Typical microstructures of the fracture surfaces as revealed by scanning electron microscopy are illustrated in Figure 6.30. The fracture surface morphology appeared very similar for cohesive failure in mild steel, nickel-aluminium and alumina coatings with a substantial part of the fracture apparently occurring between lamellae within the coatings (Figure 6.30 a-c). The differences between the coatings were mainly the presence of cracks within lamellae of the alumina coating (Figure 6.30c) whereas there was some evidence of deformation of the lamellae in both the steel and nickel aluminium coatings (Figure 6.30a-b).

The processes involved during adhesive failure were most easily observed for metal coatings (Figure 6.30d) which revealed particles completely stripped from the grit blasted substrate (at feature A) or particles which had been extensively deformed (at feature B). Adhesive failure in the case of the ceramic coating (Figure 6.30e) still took place along the interfacial boundary but the features were not as well defined as in the case of metal coatings. Some areas of the substrate were devoid of the coating material whereas others exhibited failure between the lamellae of the coating. The adhesive fracture surface between the bond coating and alumina (Figure 6.30f) exhibited areas characteristic of failure through both metal and ceramic regions.

#### 6.5.4 Discussion of Double Cantilever Beam Tests

##### 6.5.4.1 Introduction

The extensometer displacement vs force curve cannot be used to establish the fracture toughness but must be considered in conjunction with the bending of the DCB to calculate the displacement at the loading points. The extensometer compliance (equation 6.29)



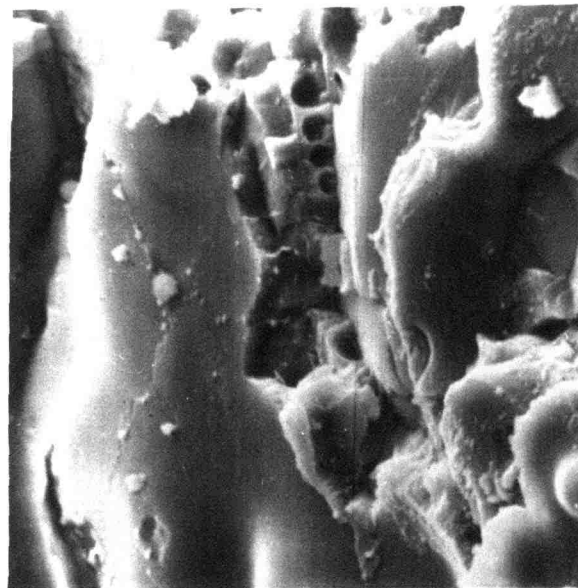
10 μm

(a) Mild steel coating



20 μm

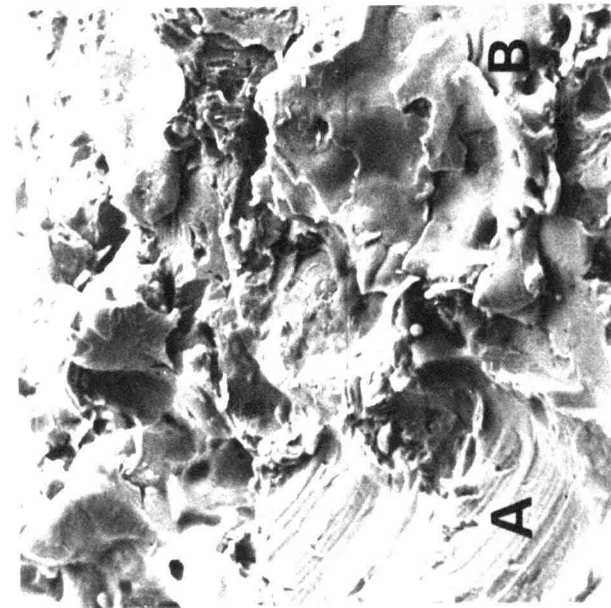
(b) Nickel-aluminium coating



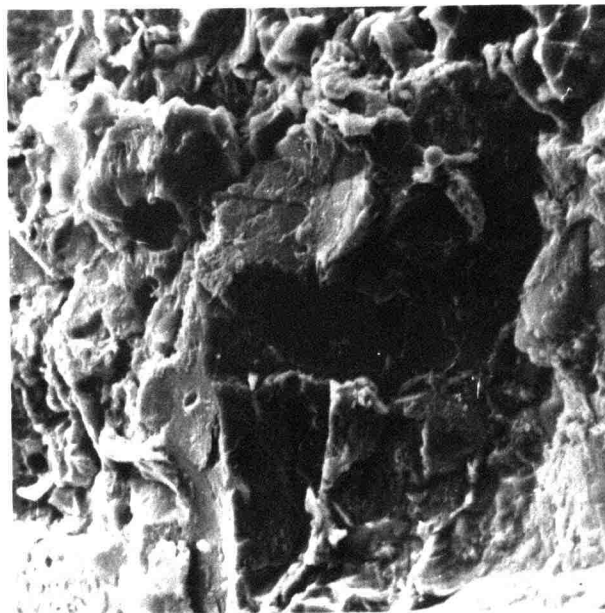
5 μm

(c) Alumina coating

Figure 6.30a-c: Cohesive failure of plasma sprayed coatings.



(d) Mild steel coating on mild steel substrate.



(e) Alumina coating on mild steel substrate.



(f) alumina coating on nickel-aluminium coating.

Figure 6.30d-f: Adhesive failure of plasma sprayed coatings.

was then used in conjunction with the bending theory of the beam (equation 6.31) to calculate the true loading point compliance (equation 6.32) so that the critical strain energy release rate could be found (equation 6.39). This has been termed the "compliance  $G_{IC}$ " in order to differentiate it from  $G_{IC}$  determined by other means.

#### 6.5.4.2 Stability of Cracking

Quasistatic cracking occurs under constant cross-head displacement conditions if the crack grows stably beyond the critical force. The force-displacement cycle is said to be reversible if crack growth ceases when the cross-head motion is stopped and the force-displacement trace returns to the origin on unloading. In the case of DCB tests carried out in this work the crack propagated after the cross-head was stopped; and sometimes the crack jumped rapidly with the displacement increasing and force decreasing. This behaviour would not occur, under the same testing procedure, if the testing equipment had a low compliance (i.e. a hard machine) since the displacement measured at the extensometer would decrease. Thus the strain energy release rate value in this work was characteristic of the initiation fracture toughness rather than that for stable crack growth.

The number of readings during a test increased with the fracture toughness value since the crack length increased significantly for the same decrement of force when testing coatings of lower fracture toughness. Figure 6.31 shows this relationship for a range of fracture toughness values and crack lengths and has been derived by applying equation 6.39. A contributing factor to large crack jumping in the ceramic coatings may be a larger initiation fracture toughness (relative to the fracture toughness for stable crack growth) in comparison to the metal coatings.

It has also been shown that the grip compliance is significant ( $2.75$  to  $4.5 \times 10^{-7} \text{ mN}^{-1}$ ) so that "soft machine" testing conditions resulted. Therefore the elastic compliance of the grips

contributed energy which enabled crack growth when the critical load was reached and the cross-head motion stopped. The crack stopped propagating at some point when the increased displacement between the loading points accommodated the diminishing strain of the grips at the lower force. If the crack grew stably between these events then the force-displacement trace formed a constant  $G_{IC}$  locus.

The area enclosed within the force-deflection curve (referred to as a curvi-linear triangle) was a measure of the energy (N-m or J) required for a crack to grow. In the majority of tests this triangle did not show reversible characteristics, where the force and displacement values would have returned to the origin after the complete cycle. The  $G_{IC}$  value calculated from the area measurement was typically less than the compliance  $G_{IC}$ . This indicates either:

- (i) the crack did not grow in a stable manner at the compliance  $G_{IC}$ ;
- (ii) the crack propagated beyond its stable crack length due to kinetic effects, or
- (iii) the linear and reversible behaviour for the loading and unloading cycle was not applicable for these tests.

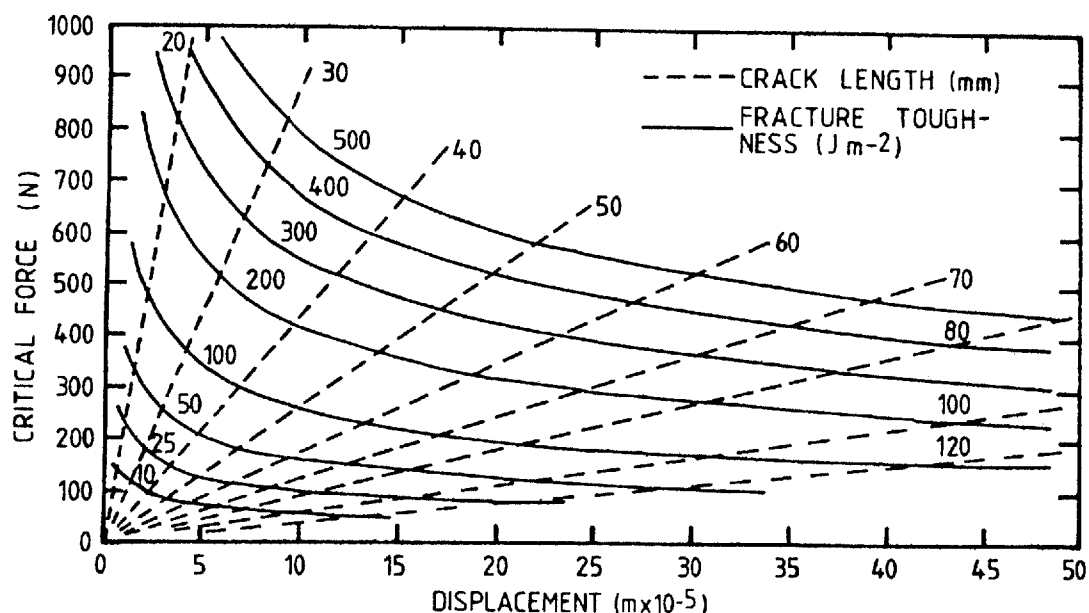


Figure 6.31: Fracture toughness related to the critical force, displacement and crack length.

Figure 6.32(a & b) shows a schematic diagram of the area calculation to account for differences that arise. The ideal loading cycle (Figure 6.32a) is reversible and the  $G_{IC}$  calculated from this area should approximate the compliance  $G_{IC}$ . If the test was not reversible (Figure 6.32b) then the area measurement includes a contribution from the displacement off-set at the end of the test; and this area is larger than that obtained from the ideal curvi-linear triangle. However the expected  $G_{IC}$  value calculated (via expression 6.26) using this area is also dependent on an accurate determination of the crack length. For example a true crack jump of 5 mm instead of 4 mm results in a 20 percent error and thus the  $G_{IC}$  value established from the true area enclosed within the trace can be larger (e.g. specimen 76 Table in 6.10) than the value calculated from the compliance measurement. On the other hand an over-estimation of the crack length can lead to a lower value of the "area  $G_{IC}$ " compared to the compliance  $G_{IC}$ . --A major source of error in these calculations is that the crack surface is not usually two dimensional but exhibits a highly deformed fracture surface which has a high surface area compared to the planar approximation.

In a number of tests both the crack jumping and the displacement off-set were large. These factors suggest that the crack growth occurred in an unstable manner from a high initiation fracture toughness. The initiation fracture toughness value derived from the compliance measurement represents the coating properties best since it

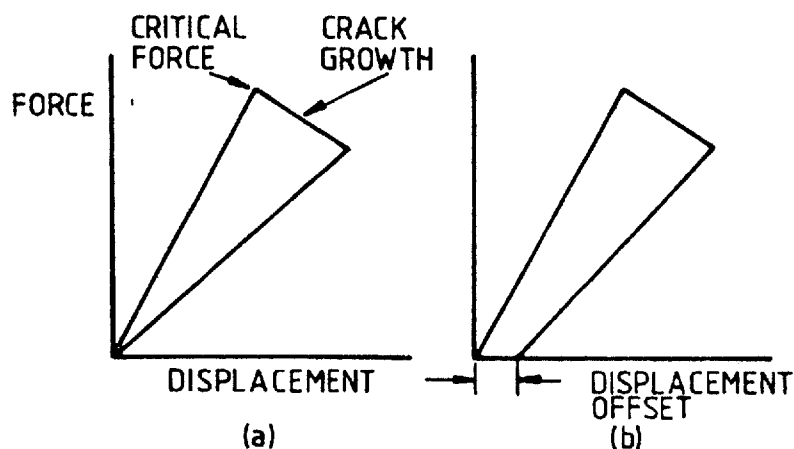


Figure 6.32: Schematic diagrams which illustrate the calculation of area enclosed by the force-displacement trace.

relates to service conditions where coatings fail in a catastrophic manner. A hard machine is most suitable for this type of test which incorporates unstable crack growth because the grip compliance does not contribute energy to the running crack after the cross-head is stopped. Therefore under test conditions the cross-head would be stopped after the onset of cracking and the crack would jump a short distance (with the displacement, measured at the extensometer, decreasing) and stop. Then the sample would be unloaded and the new crack length determined from the compliance measurement prior to another test cycle.

#### 6.5.4.3 Displacement Off-set

The displacement off-set can arise from either non-recoverable deformation of the adhesive used to manufacture the specimen (Figure 6.33a) or wedging open of the crack by particles which have plastically deformed (Figure 6.33b). For the former case Figure 6.33a shows that the compliance of the specimen is unaltered and the shaded region indicates the energy used to deform the adhesive, if it is assumed that the plastic deformation of the adhesive is a linear function of the applied force. This area does not represent energy which has been contributed to the cracking process and should not be included in any calculations to find the fracture toughness. On the other hand the crack can be wedged open and the resultant trace and correction is shown in Figure 6.33b. This area correction is approximately half of the value if plastic deformation had been assumed and also the compliance value increases. The off-set varied considerably for different coatings and generally followed a trend which is proportional to the critical force to start a crack propagating. Thus the off-set values range from large (for Ni-Al coatings), to intermediate (for mild steel coatings) to low (for alumina coatings). The compliance-crack length function levelled out at large crack lengths so that errors due to these displacements were only of major importance at short crack lengths.

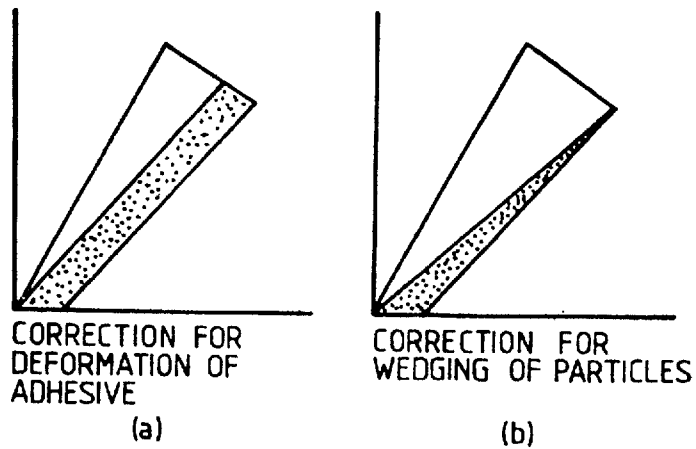


Figure 6.33: Corrections to the force-displacement curve which account for the off-set displacement.

Therefore the significance of the off-set displacement is twofold since its interpretation influences,

- (i) the measurement of the area under the force-deflection curve and
- (ii) the value of the unloading compliance and thus the final crack length.

For this work plastic deformation of the coating was observed but the correction as depicted in Figure 6.33b was not applied since the crack length was not well defined. In fact the crack may be bridged by deformed particles and in any case, as mentioned previously, the crack length correction was not significant at large compliance values.

#### 6.5.4.4 Compliance Errors and Crack Paths

The error in the crack length measurement, as obtained from the compliance curve, decreased with increasing crack length. However it was also seen from the compliance calibration that changes in crack length are determined most precisely at short lengths and thus the more reliable quantitative measurements were made at the beginning of a set of tests. Figure 6.34a shows how the absolute crack length determination

varied from fracture toughness measurements of 10 to  $410 \text{ Jm}^{-2}$  if the maximum displacement error was  $\pm 2.54 \times 10^{-6}$  ( $= 10^{-4}$  inches) and Figure 6.34b shows the relative error for the fracture toughness. While the compliance measurements established a crack length it should be kept in mind that, especially for metal coatings, this value was the mean length and extensive plastic deformation and micro-cracking may have occurred near the vicinity of the crack tip.

The cracking mode was predetermined to a large extent by grooving the DCB in the vicinity of the interface between the coating and substrate. The final profile and position of the groove was not precisely defined since it was surface ground into a coating which was only 0.5 to 1 mm thick. Consequently the root of a groove to promote adhesive failure was located in the substrate so that the cross-sectional area at the coating-substrate interface was less than the adhesive thickness. A crack then propagated at the substrate-coating interface since the coating does not have as great a fracture toughness as the substrate.

It is difficult to locate the groove root solely within the coating and expect cohesive failure because,

- (i) the coating and groove root were of similar size, and
- (ii) failure may have occurred within the adhesive when it is reduced in cross-sectional area and in the presence of micro-cracks resulting from the grooving procedure.

Cohesive failure is therefore promoted by grooving at the coating-substrate interface and scribing the central thickness of the coating with a tungsten tipped tool. Thus the main function of the groove in this case was to locally reduce the cross-sectional area of the specimen; and additional stress concentrations were provided along the expected crack path by scribing.

The crack path need not be restricted to one type during a test and was determined by the location of the groove. Thus the crack tended to propagate towards the boundary of low fracture toughness material (i.e. from cohesive to adhesive modes of failure) and this was

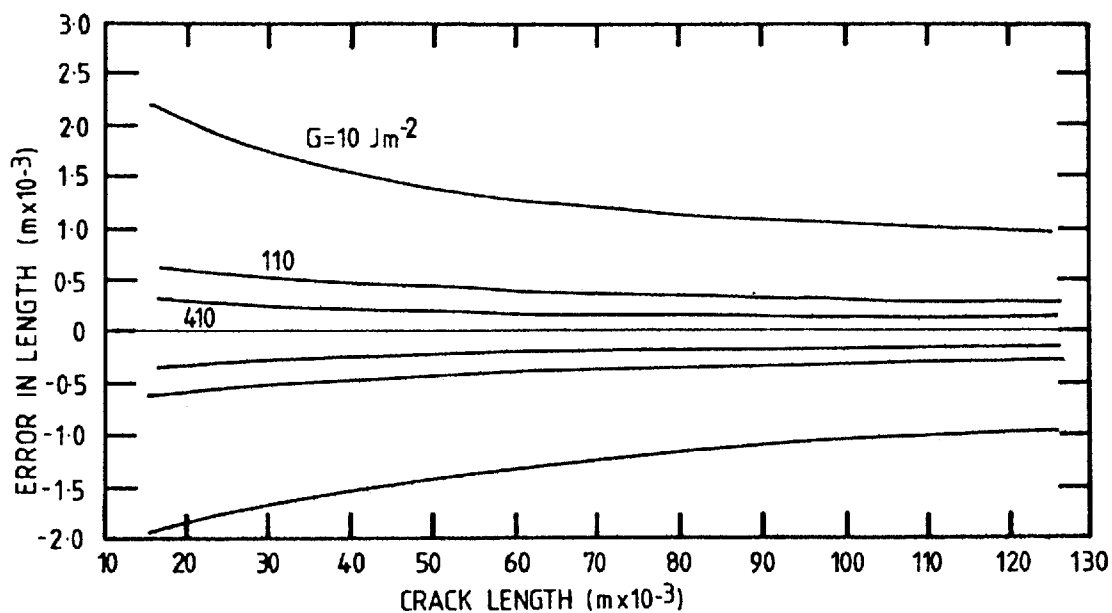


Figure 6.34a: Error in crack length measurement for various fracture toughnesses if displacement measurement is  $\pm 2.54 \times 10^{-6} \text{ m}$ .

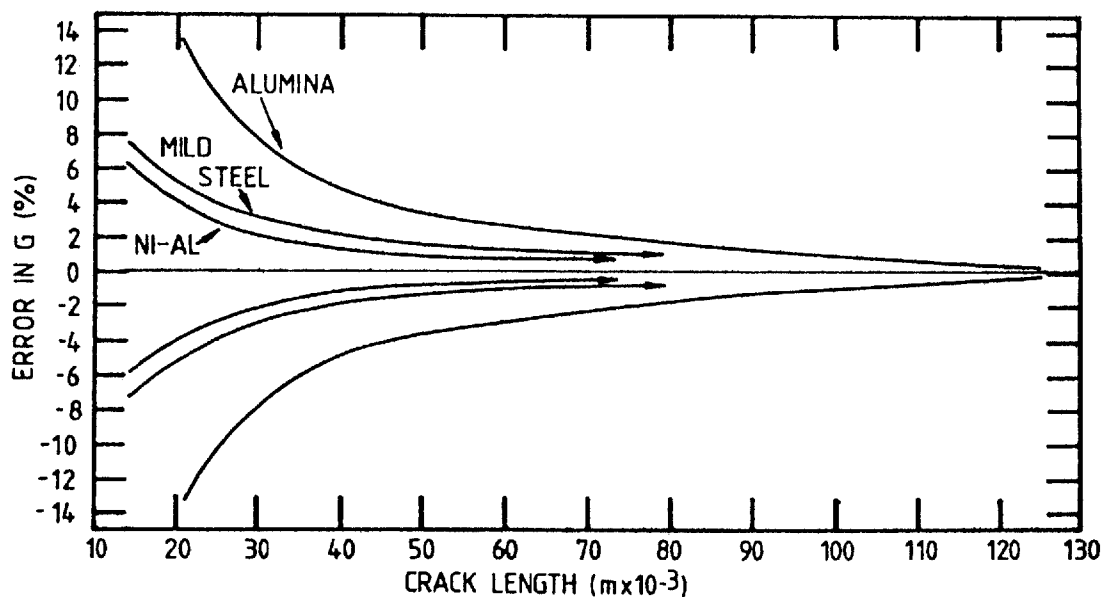


Figure 3.34b: Relative error in fracture toughness for various coatings due to errors in the crack length measurement.

reflected by a decrease in fracture toughness value with crack length. However both cracking modes were distinguished on analysis of the results and careful examination of the fracture surface.

#### 6.5.4.5 Fracture Mechanisms

The DCB results are in qualitative agreement with the generally accepted behaviour of sprayed coatings, that is the failure of alumina coatings on steel and steel on steel tend to be adhesive, rather than cohesive, and the adhesion of alumina to nickel aluminium bond coatings is superior to its adhesion to steel (Dittrich, 1965). The values obtained for the strain energy release rate for cohesive failures of alumina and steel coatings may be compared with values obtained from fracture toughness determinations on bulk specimens. The results for cohesive failure of the steel coating ( $\approx 260 \text{ Jm}^{-2}$ ) are considerably lower than those reported for brittle failure of steel of  $600\text{--}60,000 \text{ Jm}^{-2}$  (Hahn et al., 1972) and similarly the value for cohesive failure of alumina ( $21 \text{ Jm}^{-2}$ ) is lower than that reported for polycrystalline alumina of  $40\text{--}90 \text{ Jm}^{-2}$  (Wiederhorn, 1968).

These comparatively poor mechanical properties of the coatings are consistent with the lamellar microstructure of thermally sprayed coatings which arises from the process of coating formation. Molten droplets striking the substrate at high velocity ( $100\text{--}400 \text{ m sec}^{-1}$ ) flatten and solidify in microseconds, the microstructure therefore consists of layers of these individually solidified lamellae. The particle temperature and velocity distributions are quite large and the thickness of the lamellae formed, the degree of porosity because of imperfect contact between an impacting particle and previously solidified material, and the nature of the interface formed between the droplet and the surface it strikes will vary from point to point. In the case of metallic coatings the particles may partially oxidise during flight resulting in the presence of interlamellar oxide layers.

The morphology of the cohesive fracture surfaces of both metallic and ceramic coatings were similar with failure occurring predominantly between lamellae. The order of magnitude difference between the values obtained for cohesive failure of alumina and steel or nickel-aluminium can thus be ascribed to dissipation of energy in plastic deformation during crack propagation in the metallic material. The relatively high value for  $G_{IC}$  for cohesive failure of the alumina coating compared with polycrystalline alumina is also probably a result of the lamellar microstructure with complex crack branching taking place, rather than an inherently high  $G_{IC}$  for the interlamellar surface.

Microstructural examination shows that the "adhesive" failure of both  $Al_2O_3$  on steel and steel on steel are not truly adhesive, in the sense that the coating is not completely removed from the substrate at the interface, but that the crack propagates partly through the coating and partly along the interface. However the bimodal distribution of the data shows that the adhesive and cohesive fractures observed are of distinct types and may be related to practical adhesive and cohesive failure of sprayed coatings. Once again the microstructures of adhesive failures show that the crack path within the coating is predominantly between lamellae with evidence of plastic deformation in the metallic coatings. The lower values for adhesive failure than cohesive failure of both alumina and mild steel on steel substrates could have a number of interpretations, for example a difference in the "true adhesion" between lamellae and between lamellae and substrate, a difference in the fraction of area bonded between lamellae and between lamellae and substrate, differences in the geometry of the crack path or effects of residual stresses. The present study does not provide sufficient information to resolve these questions.

An interesting result is the considerably greater strain energy release rate for adhesive failure of an alumina coating on nickel-aluminium bond coat compared with alumina on steel or cohesive failure of alumina. This is in general agreement with a number of observations that alumina coatings adhere much better to nickel-aluminium than to steel (Dittrich, 1965). In this case a relatively

high fracture surface energy resulted because of plastic deformation of the metallic lamellae. This probably explains the effectiveness of a metallic bond coat on the adhesion of ceramic coatings to metals; since failure along the interface between both the substrate-bond coat and bond coat-ceramic involve plastic deformation and thus a considerable increase in fracture surface energy compared with a ceramic coating sprayed directly onto steel. In this way a graded composite structure is achieved between metallic substrate, bond coat and ceramic coating which results in superior overall coating adhesion.

#### 6.5.4.6 Features of Fracture Toughness Methods

The DCB test gave a parameter ( $G_{IC}$ ) which was related to the removal of a coating from the substrate and this parameter is more directly related to the service failure of coatings than other tests. It was also possible to examine cohesive or adhesive failures separately and it was resolved that the adhesive type of failure limited the overall adhesion of mild steel and ceramic coatings. This result would be expected since thermal and strain gradients are greatest for the initial mono-layer of deposit on the substrate and these factors would contribute to a degradation of coating properties. However the tests on bond coatings behaved in a different manner and adhesive failure was not observed presumably because the adhesive fracture toughness is greater than the cohesive fracture toughness. These different types of failure have not been critically examined before, mainly because other tests normally produce a mixed type of failure.

A significant feature of the fracture toughness method in respect to this work is that it allowed a two layer structure to be examined. Thus it was possible to restrict crack growth to the interface between the Ni-Al bond coating and the ceramic overlay, and it was found that the fracture toughness was considerably improved than the case where no bond coating was present. The fracture morphology revealed that the bond coating extensively deformed and thereby resulted in the high fracture toughness values.

It is important to distinguish the different roles that the organic adhesive has in the tensile adhesion specimens and the fracture toughness specimens. For the tensile adhesion test specimens the adhesive must have a greater tensile strength than the coating that is tested and failure of the specimen always occurs at the weakest section of the coating (or for high strength coatings within the adhesive). Usually the coating failure is complex with contributions from both the adhesive and cohesive types. However it is normally expected that one failure type is typical of a coating and the likelihood of exclusively obtaining the other failure type is slight; or if the other failure type does occur it does not represent optimum coating properties. Thus for a Ni-Al coating, which has a high adhesive strength, the testing conditions may not be appropriate to observe purely adhesive failure and this limits a study into factors controlling all the aspects of coating adhesion. On the other hand the fracture mechanics approach does not suffer from this limitation because the tensile strength of the organic adhesive is relatively unimportant compared to its own fracture toughness properties. The organic adhesives that were used had a  $G_{IC}$  of up to  $1000 \text{ Jm}^{-2}$  and thus cracking was restricted to the coating.

Another major feature of the fracture mechanics approach was that, in the case of the DCB test, many tests were carried out on one specimen so that the statistical nature of results can be mathematically treated. Thus 12 fracture toughness determinations (Table 6.8, specimen 77) were made on a single specimen and these would be expected to give a fair indication of the adhesion quality of that particular coating. The first of a series of fracture toughness measurements for a particular sample was not higher than the following determinations. This infers that the pre-cracking technique of using a jewellers saw is adequate in establishing a natural crackfront and it seems appropriate that the initiation fracture toughness is also characteristic of the energy to propagate a crack.

The major disadvantage of the DCB fracture toughness method is that specimen preparation and testing is relatively complex (and therefore costly) compared with conventional tests and it is therefore more suited to research than routine quality control.

#### 6.5.4.7 Further Work

The use of fracture toughness measurements applied to plasma spray coatings has opened up several areas of research. The testing methods described in this thesis should be applied to different plasma spray coatings so that their adhesion to the substrate can be quantitatively understood. Thus the basic mechanisms of coating formation and its structural properties can be studied by changing the substrate material, surface preparation and spraying variables.

Some variables of the coating such as deposit thickness and pre- or post- heat treatment are normally used to establish optimum coating properties as determined by the tensile adhesion test. These variables are more correctly examined in the light of causing residual stresses throughout the coating profile and the fracture mechanics method can be adopted to measuring these by prestressing the substrate prior to coating. Therefore the fracture mechanics method allows the crack path to be precisely controlled and the change in  $G_{IC}$  may be related to the sample pre-stressing operation.

Also there is no inherent disadvantage of coating failure through the most weak region because a crack path through a region of high fracture toughness can be promoted by locally reducing the cross-sectional area. However this technique was not successful for the Ni-Al coating and it would be interesting to examine completely adhesive failure in this case. Thus the failure morphology of individual particles may indicate the adhesion mechanism. The fracture behaviour can also be orientated towards the interface by choosing different materials or changing the geometry of the cantilever arms. Thus if a coating was deposited onto the less compliant arm of a DCB specimen then cracking at the interface would be expected (Becher et al., 1978).

It may also be possible to change the fracture morphology within a single specimen by ensuring that the guiding groove for the expected crack path lays entirely within the coating and also crosses the coating-substrate interface zone. It should though, be kept in

mind that if the fracture toughness of the two failure types are significantly different then large crack jumping may occur during the change from the high to the low energy fracture type. Thus both adhesive and cohesive fracture toughness values may be obtained from one specimen but the number of determinations from an individual specimen may be decreased.

The cracking stability of the DCB specimen can be improved by using less compliant grips. This would increase the number of loading cycles that could be applied to a single specimen and thus make more data available for analysis. The only component of the existing equipment that would require redesign is the specimen grips (Figure 6.20).

Several aspects of the compliance measurements also require further clarification. No precise theoretical model of the true loading point compliance as a function of crack length was derived. Instead, for this work, an exact empirical model was formulated. However it would be of interest to establish the theoretical model since this may be related to the properties of the organic adhesive and give an insight into the role of the adhesive in this particular DCB specimen. Therefore it may be found that the correction factors of  $\alpha$  and  $\beta$  proposed in equation 6.35 are related to the mechanical properties of the adhesive.

#### 6.5.4.8 Conclusions

The main areas examined in section 6.5 were the compliance measurements of DCB specimens and the fracture toughness of coatings. These studies are related and concern:-

- (1) The application of fracture toughness methods in measuring the adhesion of plasma sprayed coatings.
- (2) The significance of the fracture toughness values and the fracture morphology of plasma sprayed coatings.

The conclusions from this section are summarised below.

- (1) The DCB specimen used in this work was suitable for carrying out fracture toughness measurements.
- (2) The extensometer compliance could be related to the crack length by an empirical equation (6.29).
- (3) The deformation behaviour of the beam was critically examined so that the displacement at the loading point could be found (equation 6.31).
- (4) The compliance at the loading point ( $C_{TLP}$ ) was related to the crack length (equation 6.32) and did not fit any of the simple theories that have been proposed for cantilever bending.
- (5) Combinations of mild steel - mild steel, mild steel - aluminium and aluminium-aluminium adherends were used as the DCB arms and the compliance change with crack length established (Table 6.3).
- (6) The contribution of the grip compliance to the total compliance was significant ( $2.75$  to  $4.5 \times 10^{-7} \text{ mN}^{-1}$ ) and led to soft machine loading conditions which decreased the stability of cracking.
- (7) Grooving in the region of the coating and substrate-coating interface was used to aid either cohesive or adhesive failure respectively.
- (8) The adhesion of plasma sprayed coatings can be quantitatively expressed in terms of fracture toughness ( $G_{IC}$ ). These values were established via equation (6.39) and are summarised in Table 6.11. Coatings of Ni-Al, mild steel,  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  and a two layer coating of Ni-Al +  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$ , all sprayed onto a grit blasted mild steel substrate, were examined by the DCB technique. It was found that Ni-Al coatings adhered most strongly to

the mild steel substrate, followed by mild steel to the mild steel substrate, alumina to the Ni-Al coating and  $\text{Al}_2\text{O}_3\text{-TiO}_2$  to the mild steel substrate.

- (9) The overall coating adhesion was limited by failure at the coating-substrate interface in the cases of the alumina and mild steel coatings. Adhesive failure was not observed for the Ni-Al coating deposited onto the mild steel substrate.
- (10) The fracture toughness of a composite coating of Ni-Al and  $\text{Al}_2\text{O}_3\text{-TiO}_2$  was significantly greater than for  $\text{Al}_2\text{O}_3\text{-TiO}_2$  on steel because of the large adhesive  $G_{IC}$  at the metal-ceramic interface of the composite coating arising from deformation of the metallic lamellae.
- (11) The adhesive and cohesive failures of metal and ceramic coatings exhibited similar morphological features. The cohesive mode of failure always occurred between the lamellae of the deposited particles, as opposed to through individual particles. The metal coatings showed plastic deformation of the lamellae whereas the ceramic coatings failed in a brittle manner at the edges of lamellae. The two layer coating showed mixing of the bond and ceramic coatings over a broad zone, and failure in this region revealed plastic deformation of the Ni-Al particles.
- (12) The fracture toughness values were related to the fracture morphology. When the coating extensively deforms (i.e. for metal and Ni-Al coatings) a large amount of energy is necessary to make a crack grow and thus the adhesion of the coatings, as measured by the fracture toughness, were high compared with ceramic coatings which fracture in a brittle manner.

## APPENDIX 1

U.S. Patents Relevant to Plasma Torches  
and Plasma Spraying

|           |                                                                                                                                     |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------|
| 2,806,124 | Sept. 10, 1957, R.M. Guage (Union Carbide): "Arc Torch and Process".                                                                |
| 2,858,411 | Oct. 28, 1958, R.M. Guage (Union Carbide): "Arc Torch and Process".                                                                 |
| 2,858,412 | Oct. 28, 1958, J.S. Kane, C.W. Hill (Union Carbide): "Arc Torch".                                                                   |
| 2,922,869 | Jan. 26, 1960, G.M. Giannini, A.C. Ducati (Plasmadyne Corporation): "Plasma Stream Apparatus and Methods".                          |
| 2,960,594 | Nov. 15, 1960, M.L. Thorpe (Plasma Flame Corporation): "Plasma Flame Generator".                                                    |
| 3,016,447 | Jan. 9, 1962, R.M. Guage, O.H. Nestor, D.M. Yenni (Union Carbide): "Collimated Electric Arc-Powder Deposition Process".             |
| 3,027,447 | Mar. 27, 1962, J.A. Browning, K.W. Harrington (Thermal Dynamics Corporation): "Electric Arc Torch".                                 |
| 3,030,490 | Apr. 17, 1962, T.B. Reed (Union Carbide): "Multiple Purpose Arc Torch Apparatus".                                                   |
| 3,061,710 | Oct. 30, 1962, J.A. Browning, K.W. Harrington (Thermal Dynamics Corporation): "Electric Arc Torches".                               |
| 3,064,114 | Nov. 13, 1962, R.A. Cresswell, C.A. Burdon (The British Oxygen Company Limited): "Apparatus and Process for Spraying Molten Metal". |
| 3,106,631 | Oct. 8, 1963, R.C. Eschenbach (Union Carbide): "Arc Torch Device".                                                                  |
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| 3,106,633 | Oct. 8, 1963, G.M. Skinner, R.S. Eschenbach (Union Carbide): "Arc Torch Device".                                                    |
| 3,114,826 | Dec. 17, 1963, H.C. Sullivan, R.W. Prichard (Plasmadyne Corporation): "High-Temperature Spray Apparatus".                           |
| 3,145,287 | Aug. 18, 1964, W.A. Siebein, A.J. Rotolico (Metco Inc.): "Plasma Flame Generator and Spray Gun".                                    |

- 3,179,782 Apr. 20, 1965, L. Matvay: "Plasma Flame Jet Spray Gun with a Controlled Arc Region".
- 3,179,783 Apr. 20, 1965, R.L. Johnson (Giannini Scientific Corporation): "Method and Apparatus for Treating Electrically-Conductive Surfaces to Make Them Hard or Corrosion Resistant".
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- 3,280,295 Oct. 18, 1966, G. Mondain-Monval, G. Audric (L'Air Liquide): "Device for Projecting Pulverulent Materials by Means of a Plasma Torch".
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## APPENDIX 2

### Radiometric Definitions

#### INTRODUCTION

There are two different systems of quantities, definitions and units associated with radiation measurement. The photometric system is only meaningful over the visible portion of the spectrum (380 to 770 nm) and is established on the principle of comparing the unknown source with the energy emitted by a "standard candle". The radiometric system of classification can be applied to the entire electromagnetic spectrum and is based on the absolute SI units of joules and watts. The radiometric system is used in this thesis and will be the only system described.

#### Definitions and Terms

- (1) Wavelength - The quantity of wavelength ( $\lambda$ ) is usually expressed in units of nanometers ( $=10^{-9}$  meters) except when applied to the radiation equations (i.e. Planck's law) where the SI unit of meter is used.
- (2) Steradian - A steradian is a unit which measures a solid angle subtended at the center of a sphere by a portion of its surface. The surface area of this portion equals the square of the sphere radius.
- (3) Radiant energy (J) is energy which travels in the form of electromagnetic waves.
- (4) Radiant density ( $\text{Jm}^{-3}$ ) is the radiant energy per unit volume.
- (5) Radiant flux (W) is the radiant energy transferred per unit time. It is also referred to as "radiant power".

- (6) Radiant flux density ( $\text{Wm}^{-2}$ ) is the energy emitted per unit surface area and unit time. The term is also referred to as "radiant emittance".
- (7) Radiance ( $\text{Wm}^{-2} \text{sr}^{-1}$ ) is the radiant power that leaves a surface per unit solid angle and unit projected area of that surface.
- (8) Spectral radiance ( $\text{Wm}^{-2} \text{sr}^{-1} \text{nm}^{-1}$ ) is the radiance per unit wavelength.
- (9) Irradiance ( $\text{Wm}^{-2}$ ) is the radiant power per unit area incident upon a surface. The term differs from that of "radiant flux density" (term 6 above) because energy is emitted from a body, whereas in the case of "irradiance" energy is incident upon a surface.
- (10) Spectral irradiance ( $\text{Wm}^{-2} \text{nm}^{-1}$ ) is the irradiance per unit wavelength.
- (11) Emissivity is a numerical value for a ratio of radiometric quantities. In this thesis the emissivity is a ratio of irradiance of the specimen to the irradiance of a black body at the same temperature as the specimen.

The terms of "brightness" and "colour" temperatures should also be clearly distinguished (Pyatt, 1954). The brightness temperature is formulated from an absolute measurement over a broad wavelength range, whereas the colour temperature is a comparative measure over a range of two limited wavelengths.

## APPENDIX 3

### Calculation of Film Density from Planck's Law

This section describes how the calculations in chapter 3 were carried out to obtain Figures 3.22 and 3.23. Only the exposure calculations derived from programme 1 (up to line 700) were used in section 3.3.1 and the film density was established by using the D-log E curve for the appropriate radiation (blue or green) being analysed. For section 3.3.2 the D-log E curve was fitted to two equations with variable coefficients for either red or blue radiation (at the wavelength of maximum transmission) and these are shown in Figure A3.1. The description below explains the different parts of the programme and lists the variables. The flow chart (Figure A3.2) is a schematic of the programme logic.

#### *Lines 10 - 40*

Memory space is reserved for a number of arrays. The two dimensional arrays will hold data at 7 temperatures for up to 32 specific wavelengths. The variables are:-

- A(32,7) - spectral irradiance of a black body.
- D(32,7) - spectral irradiance which accounts for emissivity corrections.
- F(32,7) - spectral irradiance which accounts for corrections of emissivity, transmission through the filter, and the effective exposure of the film.
- H(32,7) - total irradiance (area under the curves in Figure 3.12).
- F\$(3) - file name for transmission factors of filters.
- G\$(4) - control input to continue running of the programme.
- T4 - start of temperature range.
- T5 - finish of temperature range.

*Lines 50 - 210*

Part of the spectrum is chosen for study. The files "CBR" and "CBB" hold the film sensitivity data (Table 3.3) for exposure through the red and blue filters respectively. During the usual running of the programme "CBR" is analysed first. The variables refer to:-

- X1        - start of wavelength range to be analysed.
- X2        - end of wavelength range to be analysed.
- X4)  
X5)       - data which is used to account for the shape of the D-logE curve.
- L1(25,7) - this array will initially hold the calculated film exposure times through the red filter.
- L2(25,7) - this array will hold the calculated film density through the blue filter.
- A1        - a counter which changes the calculation procedure in lines 650 to 800.

*Lines 220 to 360*

Planck's law is used to calculate the spectral irradiance

- E        - if  $E(\text{in line 320}) = E_1 + E_2$  then the emissivity of tungsten at a specific temperature and wavelength is calculated (section 3.3.1).
- if  $E = 0.35$  then the emissivity of mild steel is constant (section 3.3.2).
- D(B,C)   - matrix used to find the spectral irradiance at a range of temperatures (C) and wavelengths (B). This value incorporates a correction for the emissivity of the particle or tungsten filament.
- A(B,C)   - matrix used to find the spectral irradiance of a black body.

*Lines 380 to 450*

Tabular display of the spectral irradiance.

*Lines 480 to 560*

Correction of spectral irradiance data to account for losses through the filter and lens system of the camera. The terms refer to:-

- F(B,C) - the corrected result of D(B,C) which considers the following factors.
- T(B)/100 - transmission factor of the lens which also incorporates an allowance for the film sensitivity.
- 10 - converts the absolute data into SI units (note that a factor of  $10^{-9}$  has already been used in line 270).
- .025 - adjusts for the effective exposure time of the lens and shutter, and also converts the spectral irradiance from  $\text{Watt m}^{-2} \text{ nm}^{-1}$  to  $\text{ergs m}^{-2} \text{ nm}^{-1}$ .

*Lines 580 to 640*

Tabular display of the spectral irradiance corrected for effective exposure time, transmission of lens and film density (relative to the wavelength of maximum transmission).

*Lines 650 to 800*

The area under the spectral irradiance vs wavelength curve is calculated for a range of temperatures regardless of whether red or blue radiation is analysed. If red radiation is being examined then  $A_1=0$  and lines 660 to 700 calculate the exposure times required, over a range of temperatures, for a specific red density. The total irradiance data is used in conjunction with the equations shown in Figure A3.1 to carry out these calculations. The terms are:-

$H(X3,C)$  - total irradiance.  
 $J1$  - input red density.  
 $L1(1,C)$  - series of exposure times, at various  
 temperatures, which are required to achieve a  
 density of  $J1$ .

*Line 810*

The above calculations are carried out again for radiation transmitted through the blue filter. Since  $A1=2$  lines 720 to 790 are by-passed and only the total irradiance at several temperatures is found.

*Lines 840 to 1000*

The film density after exposure through the blue filter for exposure times of  $L1(1,C)$  (which have been calculated in lines 650 to 800) are found and stored in  $L2(1,C)$ .

*Lines 1010 to 1040*

The final tabular display is:-

$J1$  - specified red density  
 $(C*100) + (T4-100)$  - temperature  
 $L1(1,C)$  - log exposure  
 $L2(1,C)$  - film density after exposure through the blue  
 filter.  
 $L2(1,C)/J1$  - blue/red response ratio.

Thus the curves of response ratio versus exposure time for a specific red density can be drawn for a range of temperatures. The curves of response ratio versus exposure time at constant temperature can also be calculated by adjusting the programme so that the complication of choosing a constant red density (lines 720 to 790) is deleted. Thus the programme essentially calculates the film density for a range of exposures and temperatures by using the appropriate constants for red and blue radiation when necessary, and then finds the blue/red response ratio under these conditions.

## PROGRAM ONE - CALCULATION OF FILM DENSITY

```

0010 REM CBEM2DATA
0020 DIM A(32,7),D(32,7),F(32,7),H(32,7),G$(4),F$(3)
0030 LET T4=2400
0040 LET T5=3000
0050 INPUT " BLUE OR RED ?? ",F$
0060 IF F$="CBR" THEN GOTO 0150
0070 LET X1=400
0080 LET X2=500
0090 LET X3=11
0100 LET X4=2.28
0110 LET X5=1.8167
0120 DIM L2(25,7)
0130 LET A1=2
0140 GOTO 0220
0150 LET X1=590
0160 LET X2=650
0170 LET X3=7
0180 LET X4=2.48
0190 LET X5=2.0345
0200 DIM L1(25,7)
0210 LET A1=0
0220 FOR L=X1 TO X2 STEP 10
0230   LET B=(L-(X1-10))/10
0240   LET C=1
0250   FOR T=T4 TO T5 STEP 100
0260     LET N1=3.7403E-16*((L*1E-09)^-5)
0270     LET N2=(EXP(1.43879E-02/((L*1E-09)*T)))-1
0280     LET N=N1/N2
0290     LET A(B,C)=N
0300     LET E1=1.387*(L^-1.18)
0310     LET E2=(.005+(1.25E-05*L))*((2200-T)/600)
0320     LET E=.35
0330     LET D(B,C)=N*E
0340     LET C=C+1
0350   NEXT T
0360 NEXT L
0370 INPUT "START ",G$
0380 FOR B=1 TO X3
0390   FOR C=1 TO 7
0400     LET D(B,C)=D(B,C)*1E-09
0410     PRINT USING " ###. ## ",D(B,C);
0420   NEXT C
0430   PRINT USING " ### ",(B*10)+(X1-10)
0440   PRINT
0450 NEXT B
0460 OPEN FILE (0,3),F$
0470 PRINT F$
0480 FOR B=1 TO X3
0490   LET G1=(X1-10)+(10*B)
0500   PRINT G1;
0510   READ FILE (0),T(B)
0520   PRINT T(B)
0530   FOR C=1 TO 7
0540     LET F(B,C)=D(B,C)*(T(B)/100)*10*.025
0550   NEXT C
0560 NEXT B
0570 CLOSE

```

```

0580 FOR B=1 TO X3
0590   FOR C=1 TO 7
0600     PRINT USING " ###.## ",F(B,C);
0610   NEXT C
0620   PRINT USING " ### ",(B*10)+(X1-10)
0630   PRINT
0640 NEXT B
0650 FOR C=1 TO 7
0660   FOR B=X TO X3
0670     LET H1=((F(B,C)-F(B-1,C)))/2
0680     LET H2=F(B-1,C)
0690     LET H(B,C)=H1+H2+H(B-1,C)
0700   NEXT B
0710   IF A1=2 THEN GOTO 0800
0720   INPUT " RED DENS. ?? ",J1
0730   IF J1>.7 THEN GOTO 0760
0740   LET E1=((J1-.15)/.359)^(1/1.648))-X4
0750   GOTO 0770
0760   LET E1=(J1-X5)/1.0888
0770   LET E2=EXP(E1*2.303)
0780   LET L1(1,C)=E2/(1000*H(X3,C))
0790   PRINT J1,((C*100)+(T4-100)),L1(1,C)
0800 NEXT C
0810 IF A1=2 THEN GOTO 0840
0820 PRINT
0830 GOTO 0050
0840 FOR C=1 TO 7
0850   LET K=L1(1,C)
0860   PRINT USING "TEMP. = #### ",((C*100)+1800);
0870   PRINT USING "BLUE ####.##",H(X3,C);
0880   PRINT USING " EXP. T. =#^####",K;
0890   LET J2=(LOG(1000*K*H(X3,C)))/2.303
0900   IF J2>-X4 THEN GOTO 0930
0910   LET J3=.16
0920   GOTO 0980
0930   LET J3=(.359*((J2+X4))^(1.648))+.15
0940   IF J3<.7 THEN GOTO 0980
0950   LET J3=(1.0888*J2)+X5
0960   IF J3<3 THEN GOTO 0980
0970   LET J3=3
0980   PRINT USING "      DENSITY= +#.### ",J3
0990   LET L2(1,C)=J3
1000 NEXT C
1010 FOR C=1 TO 7
1020   LET L1(1,C)=LOG(L1(1,C))/2.303
1030   PRINT J1,((C*100)+(T4-100)),L1(1,C);
1035   PRINT L2(1,C),(L2(1,C)/J1)
1040 NEXT C
1050 CLOSE
1060 STOP

```

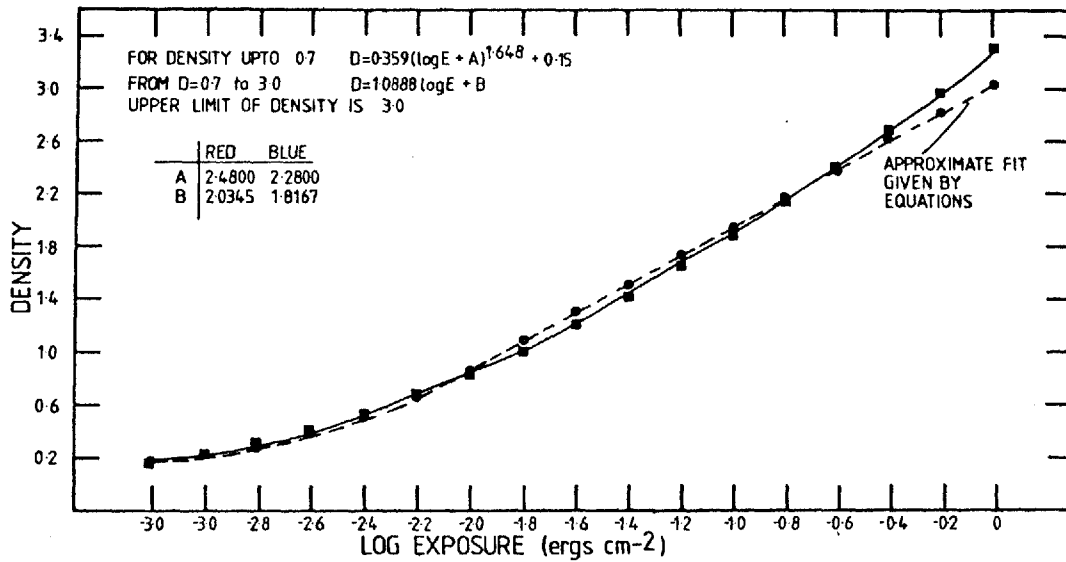


Figure A3.1: Lines of best fit for density vs log exposure curves.

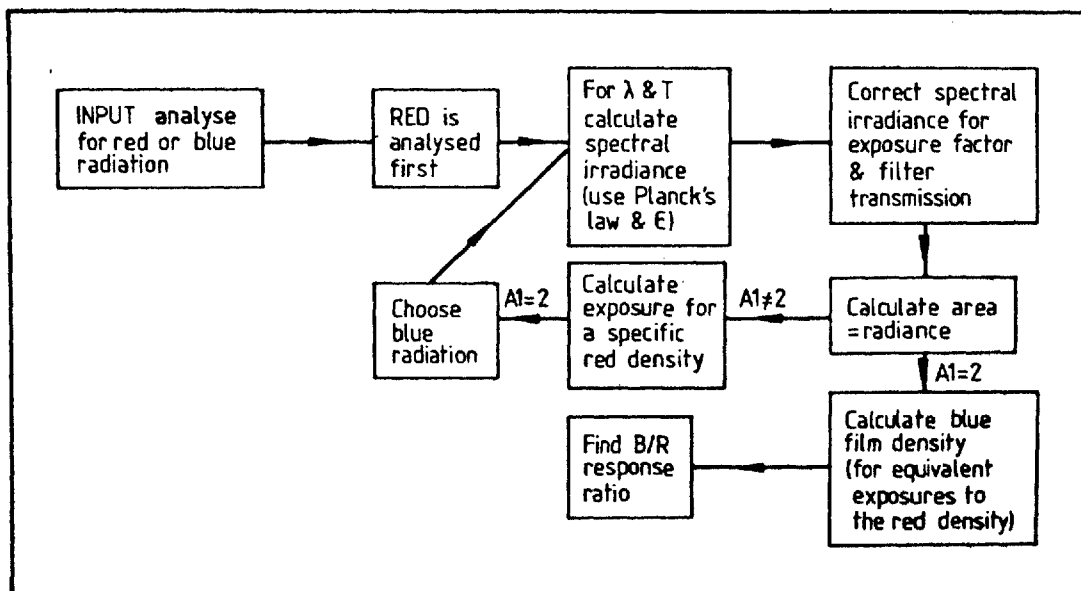


Figure A3.2: Flow chart for programme one

## APPENDIX 4

Data Collection Programme using the  
Analogue and Digital Computers

One of the programmes used for collecting data from the Instron tensile testing machine is detailed in this section. This programme was run when collecting compliance data and also typifies the procedures that were followed in running a fracture toughness test. Flexibility was incorporated into other programmes by allowing the sample rate to be changed but, for clarity, these are not described here.

There are several "CALL" commands in the programme and these have the following functions:-

- (i) CALL 35,L,S - A "control line" statement which places the output of line L into either S=1 (off) or S=0 (on) logic. These statements control two LED's so that the progress of the programme can be checked.
- (ii) CALL 51,L - A "sense line test" which controls the various stages of the programme by changing the logic via (i) above.
- (iii) CALL 42,C,V - "Analogue to digital conversion" of the force or displacement reading on channel "C". This value is denoted by the variable "V" and up to 125 readings per second can be taken.
- (iv) CALL 56,T - A "time delay" in the execution of the programme of T X 0.1 seconds.
- (v) SYS(0) - This is the computer time in seconds and is used to establish the time base for the experiment.

The programme to collect data has the following sections:

*Lines 30 to 130*

The various arrays and control statements of the programme are initialised. The variables refer to:-

X(500) - displacement measurements.  
 Y(500) - force measurements.  
 U(500) - time of the displacement and force measurements.  
 T - time interval between two measurements.  
 F\$ - data file name to be created.  
 CALL 35,0,1<sup>1</sup> - two LED's on control lines 0 and 1 are  
 CALL 35,1,1<sub>j</sub> turned off.

*Lines 140 to 160*

CALL 51,L(1) - After the initial "RUN" command the  
 programme does not continue until a  
 switch on sense line 1 is changed to  
 logic 0 (i.e. on)  
 CALL 35,0,0 - A LED on line 0 lights up and indicates  
 that the data gathering part of the  
 programme is running.

*Lines 170 to 270*

Data is recorded during an experiment. The initial time at the start of the experiment is N and the progressive time is calculated in line 230. The programme changes to the last stage when the load is less than 0 or 500 measurements have been taken.

*Lines 280 to 320*

If the allotted file space is exhausted prior to the completion of the experiment then the LED controlled by line 1 flashes on and off.

Lines 330 to 360

The time at the end of sampling is denoted by M so that the true elapsed time (M-N) can be checked with the value that is calculated by U(I). At the end of a run both LED's are alight.

#### PROGRAM TWO - DATA ACQUISITION

```

0010 REM ----- CBPROG10 -----
0020 REM --- TO FILE COMPLIANCE DATA ---
0030 DIM X(500),Y(500),U(500)
0040 DIM L(16)
0050 DIM F$(10)
0060 LET U(1)=0
0070 LET T=30
0080 PRINT "REMBER S.1 ON TO START "
0090 CALL 35,0,1
0100 CALL 35,1,1
0110 INPUT "FILENAMES ARE CBCOMP.+NO. ",F$
0120 OPEN FILE (0,1),F$
0130 PRINT "COMPLIANCE FILENAME IS ",F$
0140 CALL 51,L(1)
0150 IF L(15)=0 THEN GOTO 0140
0160 CALL 35,0,0
0170 FOR I=2 TO 500
0180   IF I>2 THEN GOTO 0200
0190   LET N=SYS(0)
0200   CALL 56,T
0210   CALL 42,6,Y(1)
0220   CALL 42,7,X(1)
0230   LET U(1)=U(1-1)+T
0240   WRITE FILE (0),I,U(1),X(1),Y(1)
0250   IF Y(1)<0 THEN GOTO 0330
0260 NEXT I
0270 CLOSE
0280 CALL 35,1,0
0290 PRINT "NO FILE SPACE LEFT"
0300 CALL 56,15
0310 CALL 35,1,1
0320 GOTO 0280
0330 LET M=SYS(0)
0340 CALL 35,1,0
0350 PRINT "TOTAL TIME= ",M-N
0360 CLOSE
0370 STOP
0380 END

```

## APPENDIX 5

## Publications

1. C.C. Berndt, R. McPherson, "Plasma Sprayed Coatings", pp.173-177 of The 8th Australian Ceramic Conference; August 15-17, 1978, Melbourne, Australia.
2. C.C. Berndt, R. McPherson, "The Adhesion of Flame and Plasma Sprayed Coatings - A Literature Review", Australian Welding Research; Jan. 1979, Vol. 6, pp. 75-85.
3. C.C. Berndt, R. McPherson, "A Fracture Mechanics Approach to the Adhesion of Plasma Sprayed Coatings", pp. 310-316 of The 9th International Thermal Spraying Conference; May 19-23, 1980, The Hague, Netherlands.
4. C.C. Berndt, R. McPherson, "A Fracture Mechanics Approach to the Adhesion of Flame and Plasma Sprayed Coatings", pp. 387-392 of The International Conference on Manufacturing Engineering; August 25-27, 1980, Melbourne, Australia.
5. C.C. Berndt, R. McPherson, "Determination of the Adhesion of Thermally Sprayed Ceramic Coatings to Metals Using Fracture Mechanics", pp. 74-81 of The 9th Australian Ceramic Conference; August 27-29, 1980, Sydney, Australia.
6. C.C. Berndt, R. McPherson, "Fracture Mechanics and Fractography of Plasma Sprayed Coatings", pp. 100-105 of The 1980 Conference of the Australian Fracture Group, November 25, 1980, Melbourne, Australia.
7. C.C. Berndt, R. McPherson, "The Adhesion of Plasma Sprayed Ceramic Coatings to Metals", Proc. 7th International Materials Symposium, Surfaces and Interfaces in Ceramics and Ceramic-Metal Systems, University of California, July, 1980. To be published in Materials Science and Research, Plenum Press, New York.

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